Visible light-induced PPh_3/MI-promoted δ-C(sp^3)-H Chlorination and Cyclization with N-chloro-arylsulfonamides via EDA Complex

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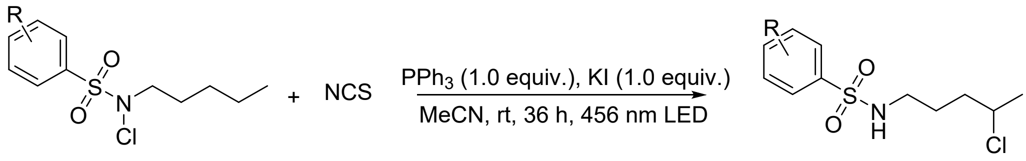
Supporting Information

1.General information

Unless otherwise noted, all reactions were carried out in flame-dried quartz tube under argon atmosphere. Anhydrous solvents were purified and dried by standard procedures. All commercially available reagents were used as received without further purification. PPh_3 and LiI were purchased from Innochem. Other reagents were purchased from Energy Chemical. Acetonitrile and acetone were distilled over P_2O_5 before use. Flash chromatography was carried out with silica gel (200-300 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. Melting points were measured on SGW® X-4 melting point apparatus and uncorrected. ^1H NMR spectra were recorded on a Bruker AVANCE III 500 spectrometer at room temperature. Chemical shifts (ppm) were referenced to tetramethylsilane (TMS, δ = 0 ppm) in $CDCl_3$ as an internal standard. $^{13}C\{^1H\}$ NMR spectra were obtained by the same NMR spectrometer and calibrated with $CDCl_3$ (δ = 77.00 ppm). ^{19}F NMR spectra were obtained by the same NMR spectrometer. Data for ^1H NMR spectra were reported as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br = broad singlet), coupling constant (Hz) and integration. Data for $^{13}C\{^1H\}$ NMR spectra were reported in terms of chemical shift and multiplicity where appropriate. High-Resolution Mass Spectrometry (HRMS) were performed on an ThermoFisher LTQ Orbitrap XL. The starting Materials **1** were obtained by previous reports [1].

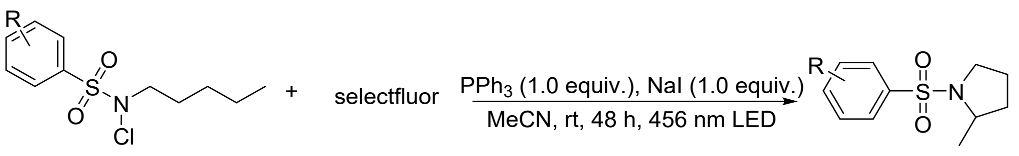
2.General procedure for synthesis of compound 2:



1 **2**

To a 25 mL of flame-dried quartz tube were added N-chloro-N-pentylbenzenesulfonamide **1** (0.5 mmol, 1.0 equiv.), N-Chlorosuccinimide (NCS) (0.9 mmol, 120.2 mg, 1.8 equiv.), PPh_3 (0.5 mmol, 131.1 mg, 1.0 equiv.), KI (0.5 mmol, 83.0 mg, 1.0 equiv.) and MeCN (2 mL). The mixture was stirred for 36 h under 3 W blue LED irradiation at room temperature in ambient air. After completion, the mixture was quenched with saturated $NaHCO_3$ (5 mL), and extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum ether to afford the desired δ-chlorosulfonamides **2**.

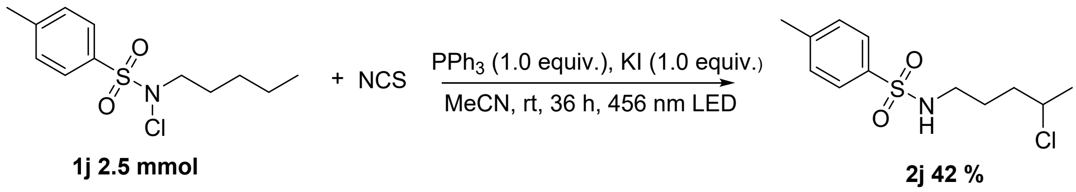
3.General procedure for synthesis of compound 3:



1 **3**

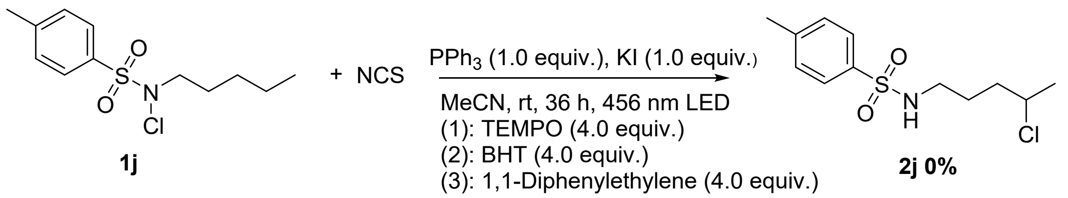
To a 25 mL of flame-dried quartz tube were added N-chloro-N-pentylbenzenesulfonamide **1** (0.5 mmol, 1.0 equiv.), selectfluor (0.9 mmol, 318.8 mg 1.8 equiv.), PPh_3 (0.5 mmol, 131.1 mg, 1.0 equiv.), NaI (0.5 mmol, 74.9 mg, 1.0 equiv.) and MeCN (2 mL). The mixture was stirred for 48 h under 3 W blue LED irradiation at room temperature under Ar atmosphere. After completion, the mixture was quenched with saturated $NaHCO_3$ (5 mL), and extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum to obtain the cycled products **3**.

4. Gram-scale reactions



To a 25 mL of flame-dried quartz tube were added N-chloro-4-methyl-N-pentylbenzenesulfonamide **1j** (2.5 mmol, 0.6877 g, 1.0 equiv.), NCS (4.5 mmol, 0.601 g, 1.8 equiv.), PPh_3 (2.5 mmol, 0.655 g 1.0 equiv.), KI (2.5 mmol, 0.415 g, 1.0 equiv.) and MeCN (8 mL). The mixture was stirred for 48 h under 6 W blue LED irradiation at room temperature in ambient air. After completion, the mixture was quenched with saturated $NaHCO_3$ (5 mL), and extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure The residue was purified by chromatography on silica gel, eluting with the mixture of ethyl acetate/petroleum to give pure products **2j** (42%).

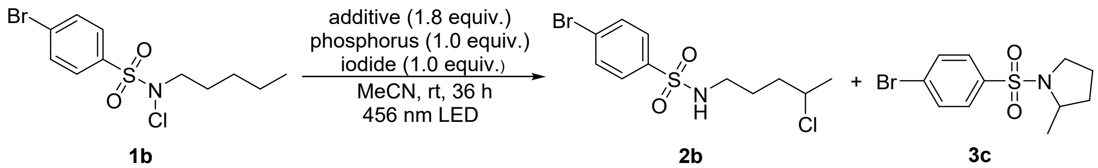
5. Mechanistic studies



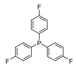
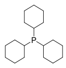
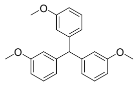
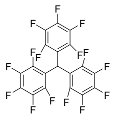
To a 25 mL of flame-dried quartz tube were added **1j** (0.5 mmol, 0.137 g, 1.0 equiv.), NCS (0.9 mmol, 120.2 mg, 1.8 equiv.), PPh_3 (0.5 mmol, 131.1 mg, 1.0 equiv.), KI (0.5 mmol, 83.0 mg, 1.0 equiv.), TEMPO (2.0 mmol, 4.0 equiv.) or BHT (2.0 mmol, 4.0 equiv.) or 1,1-Diphenylethylene (2.0 mmol, 4.0 equiv.) in MeCN (2 mL). The mixture was stirred for 36 h under 3 W blue LED irradiation at room temperature in ambient air. Product **2j** can not obtained.

6. Screening of the Reaction Conditions

Table S1 Screening of the Reaction Conditions



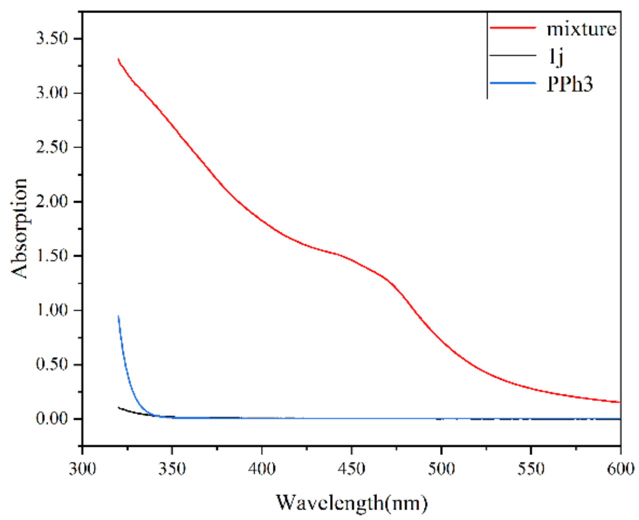
entry	additive	phosphorus source	iodine source	solvent	2b Yield (%)[g]	2c Yield (%)[g]
1	NCS	PPh_3	KI	MeCN	48	---

2	---	PPh_3	KI	MeCN	$<$10	---
3	NCS	PPh_3	CsI	MeCN	33	---
4	NCS	PPh_3	NaI	MeCN	0	$<$10
5	NCS		KI	MeCN	15	---
6	NCS		KI	MeCN	0	---
7	NCS		KI	MeCN	16	---
8	NCS		KI	MeCN	20	---
9	NCS	PPh_3	KI (0.5 equiv.)	MeCN	20	---
10	NCS	PPh_3 (0.5 equiv.)	KI	MeCN	23	---
11	NCS	PPh_3	KI	CH_2Cl_2	30	---
12	NCS	PPh_3	KI	DMF	0	---
13[b]	NCS	PPh_3	KI	MeCN	0	---
14[c]	NCS	PPh_3	KI	MeCN+ 3Å MS	50	---
15	NCS	PPh_3	KI	MeCN+H_2O	25	---
16[d]	NCS	PPh_3	KI	MeCN	53	---
17	seletfluor	PPh_3	NaI	MeCN	---	20
18	CuI	PPh_3	NaI	MeCN	---	0
19	AgF	PPh_3	NaI	MeCN	---	0

20	seletfluor	PPh_3	NaI	Ethyl ether	---	14
21	seletfluor	PPh_3	NaI	THF	---	0
22	seletfluor	PPh_3	NaI	CH_2Cl_2	---	15
23[e]	seletfluor	PPh_3	NaI	MeCN	---	0
24[f]	seletfluor	PPh_3	NaI	MeCN	---	16

[a] Reaction conditions: **1a** (0.50 mmol, 1.0 equiv.), additive (0.90 mmol, 1.8 equiv.), iodine (0.50 mmol, 1.0 equiv.), phosphorus (0.50 mmol, 1.0 equiv.), MeCN (2.0 mL) at room temperature under LED irradiation (3.0 W) in argon. [b] Dark conditions. [c] dried molecular sieve. [d] Under ambient air. [e] Dark conditions. [f] Under ambient air. [g] Isolated yield

7. The absorption spectra of individual compounds and mixture[a]

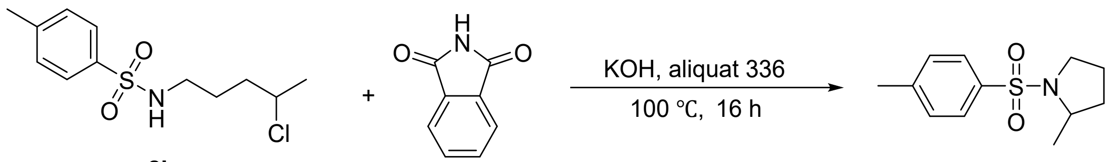


[a] Optical absorption spectra recorded in a 1 cm path quartz cuvettes using a Shimadzu UV-1800 UV-visible spectrophotometer. b mixture = 1j, KI and PPh_3

Figure S1 the absorption spectra of individual compounds and mixture

The PPh_3 sample is 0.01 M in 2.00 mL MeCN. **1j** is 0.01 M in 2.00 mL MeCN. The mixed sample is **1j** (0.01 M), PPh_3 (0.01 M), KI (0.01 M) in 2.00 mL MeCN. The samples were tested after 1 hour of sonication. Then the solutions were measured in a quartz cuvette with a UV-Vis spectrometer. The parameters were shown below: Scan range: 400-600 nm; scan rate: 60 nm/min; smooth: 6 nm; slit: 1 nm.

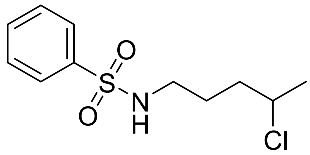
8. Derivatization Experiments



2j

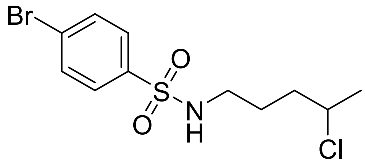
To a 25 mL of flame-dried Schlenk flask were added product **2j** (0.1 mmol, 1.0 equiv.), phthalimide (0.1 mmol, 1. 0 equiv.), KOH (0.12 mmol, 1.2 equiv.), Methyltrioctylammonium chloride (aliquat 336) (0.025 mmol, 0.25 equiv.) and MeCN (2 mL) under argon atmosphere. The reaction mixture was stirred at 100 °C (oil bath temperature) for 16 h. After the reaction was completed as indicated by TLC, the system was quenched with water (50 mL), and extracted with ethyl acetate (10 mL × 3). The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The resulting crude products were purified by silica gel chromatography to give pure product in 93% yield.

9.Spectroscopic data



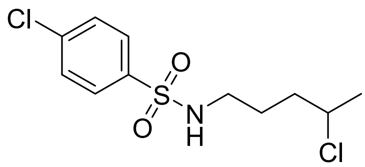
N-(4-chloropentyl)benzenesulfonamide(2a)

Yellow oil. R_f = 0.35 (petroleum ether/EtOAc = 5:1); 60 mg (46%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.4 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.53 (t, *J* = 7.5 Hz, 2H), 4.69 (t, *J* = 5.8 Hz, 1H), 3.99-3.92 (m, 1H), 2.99 (q, *J* = 6.4 Hz, 2H), 1.76-1.60 (m, 4H), 1.46 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.9, 132.7, 129.2, 127.0, 57.9, 42.7, 37.0 26.8, 25.3. Analytical data were in accordance with the literature[1a].



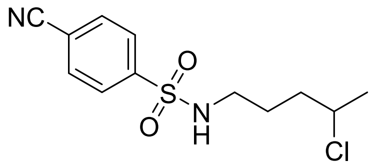
4-bromo-N-(4-chloropentyl)benzenesulfonamide(2b)

Yellow oil. R_f = 0.32 (petroleum ether/EtOAc = 5:1); 89 mg (53%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 4.53 (s, 1H), 4.01-3.94 (m, 1H), 3.00 (q, *J* = 6.3 Hz, 2H), 1.77-1.58 (m, 4H), 1.48 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.0, 132.5, 128.6, 127.7, 57.8, 42.7, 37.0, 26.8, 25.4. Analytical data were in accordance with the literature[2].



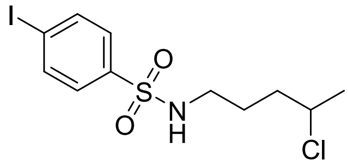
4-chloro-N-(4-chloropentyl)benzenesulfonamide(2c)

Yellow oil. R_f = 0.37 (petroleum ether/EtOAc = 5:1); 81 mg (55%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 4.63 (t, *J* = 5.8 Hz, 1H), 4.01-3.92 (m, 1H), 2.99 (q, *J* = 6.3 Hz, 2H), 1.78-1.57 (m, 4H), 1.48 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 138.4, 129.5, 128.5, 57.8, 42.7, 36.9, 26.8, 25.4. Analytical data were in accordance with the literature[2].



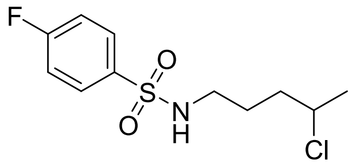
N-(4-chloropentyl)-4-cyanobenzenesulfonamide(2d)

Yellow oil. R_f = 0.58 (petroleum ether/EtOAc = 3:1); 75 mg (53%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 4.92 (t, *J* = 6.1 Hz, 1H), 4.01-3.94 (m, 1H), 3.03 (q, *J* = 6.3Hz, 2H), 1.78-1.58 (m, 4H), 1.48 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.3, 133.03, 133.00, 127.6, 117.2, 116.4, 57.8, 42.8, 36.8, 26.8, 25.3. Analytical data were in accordance with the literature[2].



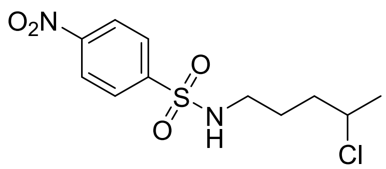
N-(4-chloropentyl)-4-iodobenzenesulfonamide(2e)

Yellow oil. R_f = 0.35 (petroleum ether/EtOAc = 5:1); 79 mg (41%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.89 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.58 (d, *J* = 8.5 Hz, 2H), 4.77 (s, 1H), 4.01-3.93 (m, 1H), 2.98 (q, *J* = 6.3 Hz, 2H), 1.78-1.56 (m, 4H), 1.47 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.76, 138.4, 128.4, 100.0, 57.8, 42.7, 36.9, 26.8, 25.4; HRMS (ESI-TOF) m/z $[M + Na]^+$ calculated for $C_{11}H_{15}NO_2NaSClI^+$: 409.9454, found: 409.9457.



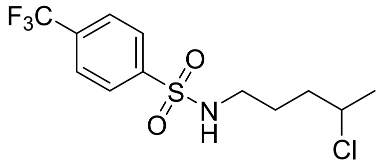
N-(4-chloropentyl)-4-fluorobenzenesulfonamide(2f)

Yellow oil. R_f = 0.62 (petroleum ether/EtOAc = 3:1); 60 mg (43%); ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (q, *J* = 4.6 Hz, 2H), 7.14 (t, *J* = 8.5 Hz, 2H), 4.29 (s, 1H), 3.95-3.86 (m, 1H), 2.97-2.87 (m, 2H), 1.72-1.55 (m, 4H), 1.42 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1 (d, *J* = 255.1 Hz), 136.0, 129.8 (d, *J* = 9.4 Hz), 116.4 (d, *J* = 22.6 Hz), 57.9, 42.7, 37.0, 26.8, 25.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -105.21. Analytical data were in accordance with the literature[2].



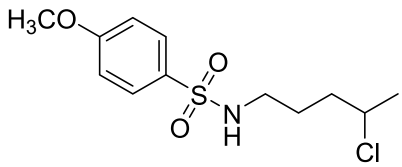
N-(4-chloropentyl)-4-nitrobenzenesulfonamide(2g)

Yellow oil. R_f = 0.28 (petroleum ether/EtOAc = 5:1); 67 mg (44%); ^1H NMR (500 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.7 Hz, 2H), 7.99 (d, *J* = 8.7 Hz, 2H), 4.50 (s, 1H), 3.96-3.87 (m, 1H), 3.00 (q, *J* = 6.0 Hz, 2H), 1.73-1.55 (m, 4H), 1.43 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 150.1, 145.8, 128.3, 124.4, 57.8, 42.8, 36.8, 26.8, 25.3. Analytical data were in accordance with the literature[2].



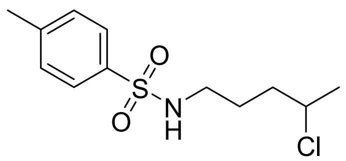
N-(4-chloropentyl)-4-(trifluoromethyl)benzenesulfonamid(2h)

Yellow oil. R_f = 0.37 (petroleum ether/EtOAc = 5:1); 67 mg (41%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, J = 8.2 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 4.81 (t, J = 6.0 Hz, 1H), 4.00-3.93 (m, 1H), 3.03 (q, J = 6.3 Hz, 2H), 1.78-1.58 (m, 4H), 1.47 (d, J = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.6, 134.5 (q, J = 33.2 Hz), 127.5, 126.4 (q, J = 3.6 Hz), 123.2 (q, J = 272.8 Hz), 57.8, 42.8, 36.9, 26.8, 25.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.74. Analytical data were in accordance with the literature[2].



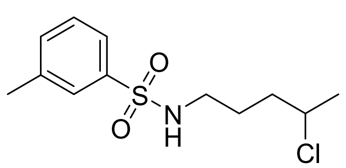
N-(4-chloropentyl)-4-methoxybenzenesulfonamide(2i)

Yellow oil. R_f = 0.52 (petroleum ether/EtOAc = 3:1); 49 mg (34%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 8.8 Hz, 2H), 6.99 (d, J = 8.8 Hz, 2H), 4.30 (s, 1H), 4.01-3.93 (m, 1H), 3.88 (s, 3H), 2.97 (q, J = 6.4 Hz, 2H), 1.78-1.57 (m, 4H), 1.48 (d, J = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 163.0, 131.5, 129.2, 114.3, 58.0, 55.6, 42.6, 37.0, 26.7, 25.4. Analytical data were in accordance with the literature[2].



N-(4-chloropentyl)-4-methylbenzenesulfonamide(2j)

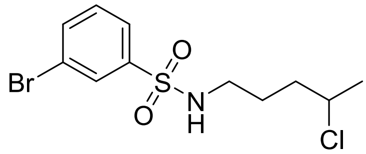
Yellow oil. R_f = 0.24 (petroleum ether/EtOAc = 5:1); 66 mg (48%);^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.53 (s, 1H), 4.00-3.92 (m, 1H), 2.97 (q, J = 6.4 Hz, 2H), 2.43 (s, 3H), 1.79-1.55 (m, 4H), 1.47 (d, J = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.5, 136.9, 129.7, 127.1, 58.0, 42.6, 37.0, 26.7, 25.3, 21.5. Analytical data were in accordance with the literature[2].



N-(4-chloropentyl)-3-methylbenzenesulfonamide(2k)

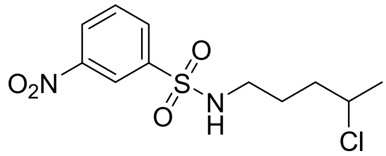
Yellow oil. R_f= 0.37 (petroleum ether/EtOAc = 5:1); 44 mg (32%); ^{1}H NMR (500 MHz, $CDCl_3$) δ

7.73-7.61 (m, 2H), 7.44-7.34 (m, 2H), 4.53 (t, *J* = 5.9 Hz, 1H), 4.02-3.91 (m, 1H), 2.99 (q, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 1.81-1.59 (m, 4H), 1.47 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 139.4, 133.5, 129.0, 127.4, 124.2, 57.9, 42.7, 37.0, 26.8, 25.3, 21.3; HRMS (ESI-TOF) m/z $[M + Na]^+$ calculated for $C_{12}H_{18}NO_2NaSCl^+$: 298.0644, found: 298.0643.



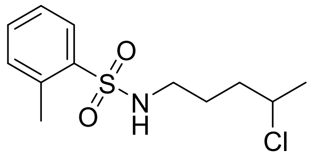
3-bromo-N-(4-chloropentyl)benzenesulfonamide(2l)

Yellow oil. Rf = 0.32 (petroleum ether/EtOAc = 5:1); 66 mg (39%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.78 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.9 Hz, 1H), 4.37 (t, *J* = 5.6 Hz, 1H), 4.01-3.91 (m, 1H), 3.05-2.95 (m, 2H), 1.79-1.56 (m, 4H), 1.48 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.9, 135.8, 130.7, 130.0, 125.6, 123.2, 57.8, 42.8, 37.0, 26.8, 25.4. Analytical data were in accordance with the literature[2].



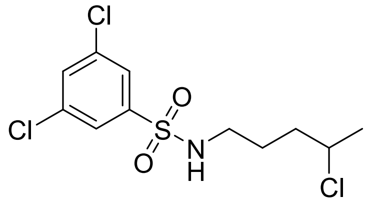
N-(4-chloropentyl)-3-nitrobenzenesulfonamide(2m)

Yellow oil. R_f = 0.55 (petroleum ether/EtOAc = 3:1); 36 mg (24%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (t, *J* = 1.8 Hz, 1H), 8.37 (dd, *J* = 8.0, 1.5 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 4.62 (t, *J* = 6.0 Hz, 1H), 3.95-3.87 (m, 1H), 3.01 (q, *J* = 6.2 Hz, 2H), 1.73-1.51 (m, 4H), 1.42 (d, *J* = 6.6 Hz, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.4, 142.3, 132.5, 130.6, 127.2, 122.2, 57.8, 42.9, 36.9, 26.9, 25.4; HRMS (ESI-TOF) m/z $[M + Na]^+$ calculated for $C_{11}H_{15}N_2O_4NaSCl^+$: 329.0339, found: 329.0343.



N-(4-chloropentyl)-2-methylbenzenesulfonamide(2n)

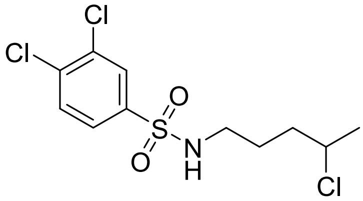
Yellow oil. R_f= 0.35 (petroleum ether/EtOAc = 5:1); 34 mg (25%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98-7.96 (m, 1H), 7.48-7.44 (m, 1H), 7.34-7.30 (m, 2H), 4.39 (d, *J* = 6.0 Hz, 1H), 3.97-3.90 (m, 1H), 2.98 (q, *J* = 6.4 Hz, 2H), 2.65 (s, 3H), 1.55-1.76 (m, 4H), 1.46 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 136.9, 132.8, 132.6, 129.5, 126.2, 57.8, 42.5, 37.0, 26.9, 25.3, 20.3. Analytical data were in accordance with the literature[3].



3,5-dichloro-N-(4-chloropentyl)benzenesulfonamide(2p)

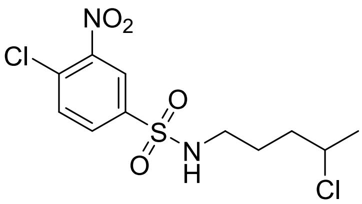
Yellow oil. R_f = 0.54 (petroleum ether/EtOAc = 5:1); 44 mg (27%); ^{1}H NMR (500 MHz, $CDCl_3$)

δ 7.67 (d, *J* = 1.6 Hz, 2H), 7.49 (s, 1H), 4.47 (d, *J* = 5.5 Hz, 1H), 3.96-3.88 (m, 1H), 2.98 (q, *J* = 6.3 Hz, 2H), 1.74-1.53 (m, 4H), 1.43 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.0, 136.2, 132.7, 125.4, 57.8, 42.9, 36.9, 26.8, 25.4; HRMS (ESI-TOF) m/z $[M + Na]^+$ calculated for $C_{11}H_{14}NO_2NaSCl_3{}^+$: 351.9709, found: 351.9716.



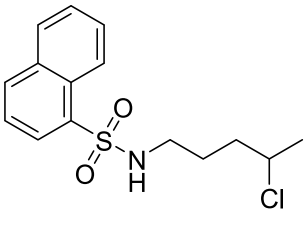
3,4-dichloro-N-(4-chloropentyl)benzenesulfonamide(2q)

Yellow oil. R_f = 0.54 (petroleum ether/EtOAc = 5:1); 50 mg (31%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (s,1H), 7.62 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.54 (d, *J* = 8.5 Hz, 1H), 4.51 (t, *J* = 5.8 Hz, 1H), 3.96-3.87 (m, 1H), 2.96 (q, *J* = 6.2 Hz, 2H), 1.74-1.50 (m, 4H), 1.42 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.8, 137.6, 133.9, 131.2, 129.0, 126.1, 57.8, 42.8, 36.9, 26.8, 25.4; HRMS (ESI-TOF) m/z $[M + Na]^+$ calculated for $C_{11}H_{14}NO_2NaSCl_3{}^+$: 351.9709, found: 351.9708.



4-chloro-N-(4-chloropentyl)-3-nitrobenzenesulfonamide(2r)

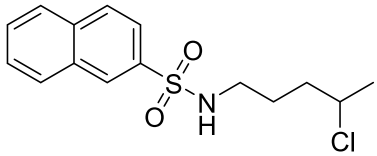
Yellow oil. R_f = 0.63 (petroleum ether/EtOAc = 3:1); 34 mg (20%);^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (s, 1H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 4.71 (t, *J* = 5.8 Hz, 1H), 4.05-3.94 (m, 1 H), 3.07 (q, *J* = 6.0 Hz, 1 H), 1.82-1.71 (m, 2H), 1.71-1.64 (m, 2H), 1.50 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 148.0, 140.4, 133.0, 131.7, 131.0, 124.3, 57.8, 42.9, 36.9, 26.8, 25.4; HRMS (ESI-TOF) m/z $[M + Na]^+$ calculated for $C_{11}H_{14}N_2O_4NaSCl_2{}^+$: 362.9949, found: 362.9944.



N-(4-chloropentyl)naphthalene-1-sulfonamide(2s)

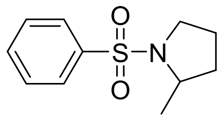
Yellow oil. R_f = 0.31 (petroleum ether/EtOAc = 5:1); 62 mg (40%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.6 Hz, 1H), 8.22 (d, *J* = 7.3 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.91 (d, *J* = 8.2 Hz, 1H), 7.65-7.62 (m, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 4.67 (s, 1H), 3.79-3.70 (m, 1H), 2.89 (q, *J* = 6.1 Hz, 2H), 1.59-1.50 (m, 2H), 1.48-1.39 (m, 2H), 1.28 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.5, 134.3, 134.3, 129.7, 129.2, 128.4, 128.2, 126.9, 124.3, 124.2, 57.8, 42.7, 36.8, 26.7, 25.2; HRMS (ESI-TOF) m/z $[M + Na]^+$ calculated for

$C_{15}H_{18}NO_2NaSCl^+$: 334.0644, found: 334.0649.



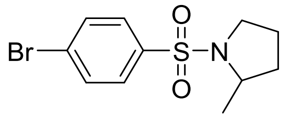
N-(4-chloropentyl)naphthalene-2-sulfonamide(2t)

Yellow oil. Rf = 0.61 (petroleum ether/EtOAc = 3:1); 66 mg (43%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (s, 1H), 7.98 (d, J = 2.0 Hz, 1H), 7.96 (s, 1H), 7.84 (dd, J = 8.5, 1.5 Hz, 1H), 7.63-7.59 (m, 2H), 4.67 (t, J = 6.1 Hz, 1H), 3.96-3.92 (m, 1H), 3.02 (q, J = 6.3 Hz, 2H), 1.76-1.57 (m, 4H), 1.43 (d, J = 6.6 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.7, 134.8, 132.2, 129.6, 129.2, 128.8, 128.4, 127.9, 127.6, 122.2, 57.9, 42.7, 37.0, 26.8, 25.3. Analytical data were in accordance with the literature[1a].



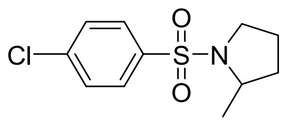
2-methyl-1-(phenylsulfonyl)pyrrolidine(3a)

Yellow oil.R_f = 0.46 (petroleum ether/EtOAc = 5:1); 50 mg (45%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78-7.76 (m, 2H), 7.53-7.47 (m, 1H), 7.45 (t, J = 7.6 Hz, 2H), 3.70-3.63 (m, 1H), 3.40-3.34 (m, 1H), 3.14-3.07 (m, 1H), 1.81-1.71 (m, 1H), 1.66-1.58 (m, 1H), 1.51-1.39 (m, 2H), 1.25 (d, J = 6.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.9, 132.4, 129.0, 127.4 , 56.2, 49.0, 33.5, 23.9, 22.8. Analytical data were in accordance with the literature[4].



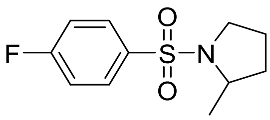
1-((4-bromophenyl)sulfonyl)-2-methylpyrrolidine(3b)

Yellow oil.Rf = 0.56 (petroleum ether/EtOAc = 5:1); 30 mg (20%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, J = 8.5 Hz, 2H), 7.58 (d, J = 8.5 Hz, 2H), 3.68-3.60 (m, 1H), 3.40-3.34 (m, 1H), 3.10-3.03 (m, 1H), 1.84-1.74 (m, 1H), 1.70-1.62 (m, 1H), 1.55-1.41 (m, 2H), 1.24 (d, J = 6.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.0, 132.2, 128.9, 127.4, 56.3, 49.0, 33.5, 23.9, 22.8. Analytical data were in accordance with the literature[4].



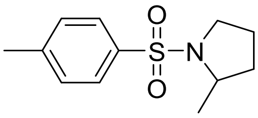
1-((4-chlorophenyl)sulfonyl)-2-methylpyrrolidine(3c)

Yellow oil.R_f = 0.66 (petroleum ether/EtOAc = 3:1); 20 mg (16%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 3.68-3.61 (m, 1H), 3.40-3.35 (m, 1H), 3.11-3.04 (m, 1H), 1.83-1.74 (m, 1H), 1.70-1.62 (m, 1H), 1.55-1.49 (m, 1H), 1.47-1.41 (m, 1H), 1.24 (d, J = 6.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.9, 136.7, 129.3, 128.8, 56.3, 49.0, 33.5, 23.9, 22.7. Analytical data were in accordance with the literature[5].



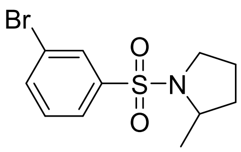
1-((4-fluorophenyl)sulfonyl)-2-methylpyrrolidine(3d)

Yellow oil.R_f = 0.51 (petroleum ether/EtOAc = 5:1); 23 mg (19%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81-7.76 (m, 2H), 7.15-7.09 (m, 2H), 3.68-3.61 (m, 1H), 3.39-3.34 (m, 1H), 3.10-3.04 (m, 1H), 1.83-1.74 (m, 1H), 1.69-1.61 (m, 1H), 1.54-1.41 (m, 2H), 1.24 (d, J = 6.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.0 (d, J = 254.3 Hz), 134.3 (d, J = 3.0 Hz), 130.0 (d, J = 9.2 Hz), 116.2 (d, J = 22.7 Hz), 56.2, 49.0, 33.5, 23.9, 22.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -105.85. Analytical data were in accordance with the literature[5].



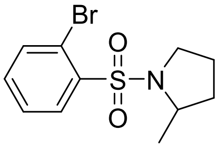
2-methyl-1-tosylpyrrolidine(3e)

Yellow oil.R_f = 0.67 (petroleum ether/EtOAc = 3:1); 20 mg (17%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.0 Hz, 2H), 3.67-3.60 (m, 1H), 3.39-3.33 (m, 1H), 3.11-3.04 (m, 1H), 2.35 (s, 3H), 1.80-1.70 (m, 1H), 1.67-1.57 (m, 1H), 1.50-1.37 (m, 2H), 1.24 (d, J = 6.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.1, 134.9, 129.5, 127.4 , 56.1, 49.0, 33.4, 23.9, 22.9, 21.5. Analytical data were in accordance with the literature[5].



1-((3-bromophenyl)sulfonyl)-2-methylpyrrolidine(3f)

Yellow oil.R_f = 0.51 (petroleum ether/EtOAc = 5:1); 33 mg (22%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 3.80-3.69 (m, 1H), 3.52-3.41 (m, 1H), 3.19-3.14 (m, 1H), 1.93-1.82 (m, 1H), 1.79-1.69 (m, 1H), 1.64-1.57 (m, 1H), 1.57-1.48 (m, 1H), 1.32 (d, J = 6.3 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.9, 135.5, 130.5, 130.2, 125.9, 123.1, 56.3, 49.1, 33.5, 23.9, 22.8; HRMS (ESI-TOF) m/z $[M + Na]^+$ calculated for $C_{11}H_{14}NO_2NaSBr^+$: 325.9826, found: 325.9831.



1-((2-bromophenyl)sulfonyl)-2-methylpyrrolidine(3g)

Yellow oil.R_f = 0.35 (petroleum ether/EtOAc = 3:1); 19 mg (13%); ^{1}H NMR (500 MHz, $CDCl_3$), 8.06 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H) δ 4.06-3.97 (m, 1H), 3.48-3.40 (m, 1H), 3.40-3.33 (m, 1H), 2.02-1.93 (m, 1H), 1.93-1.84 (m, 1H), 1.81-1.71 (m, 1H), 1.60-1.53 (m, 1H), 1.10 (d, J = 6.4 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.6, 135.6, 133.2, 132.1, 127.5, 120.5, 56.2, 48.5, 33.9, 24.1, 21.6; HRMS (ESI-TOF) m/z [M +

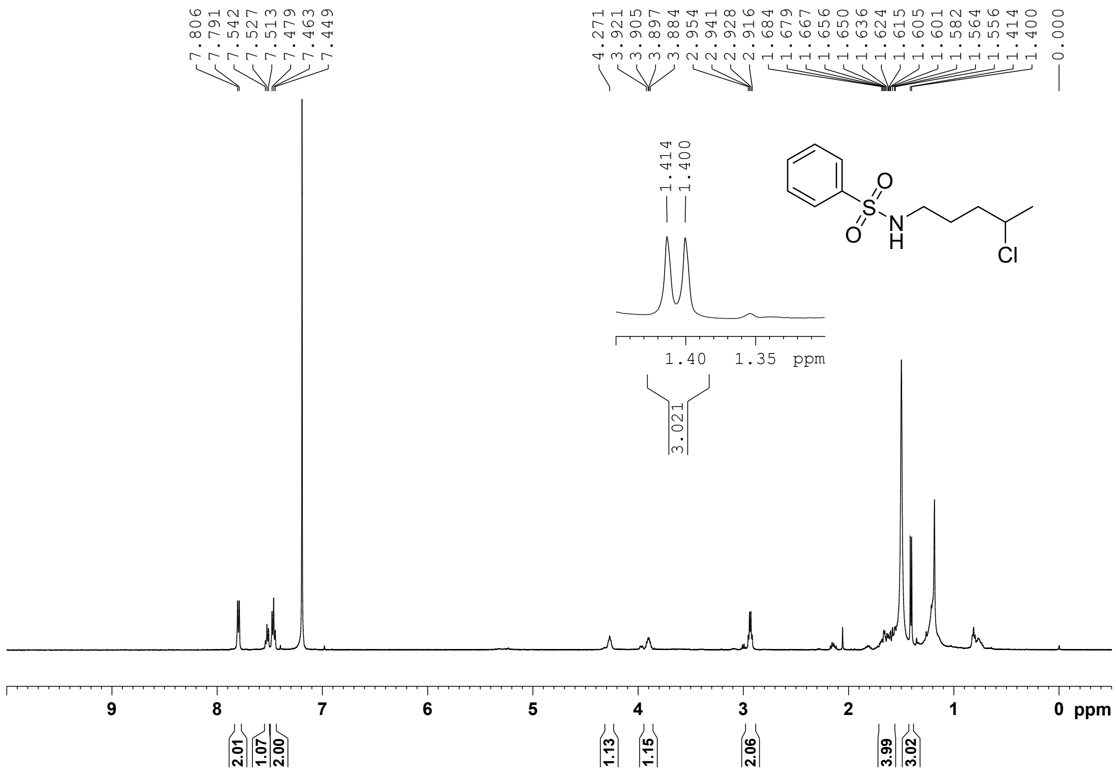
Na]$^+$ calculated for $C_{11}H_{14}NO_2NaSBr^+$: 325.9826, found: 325.9829.

10. References

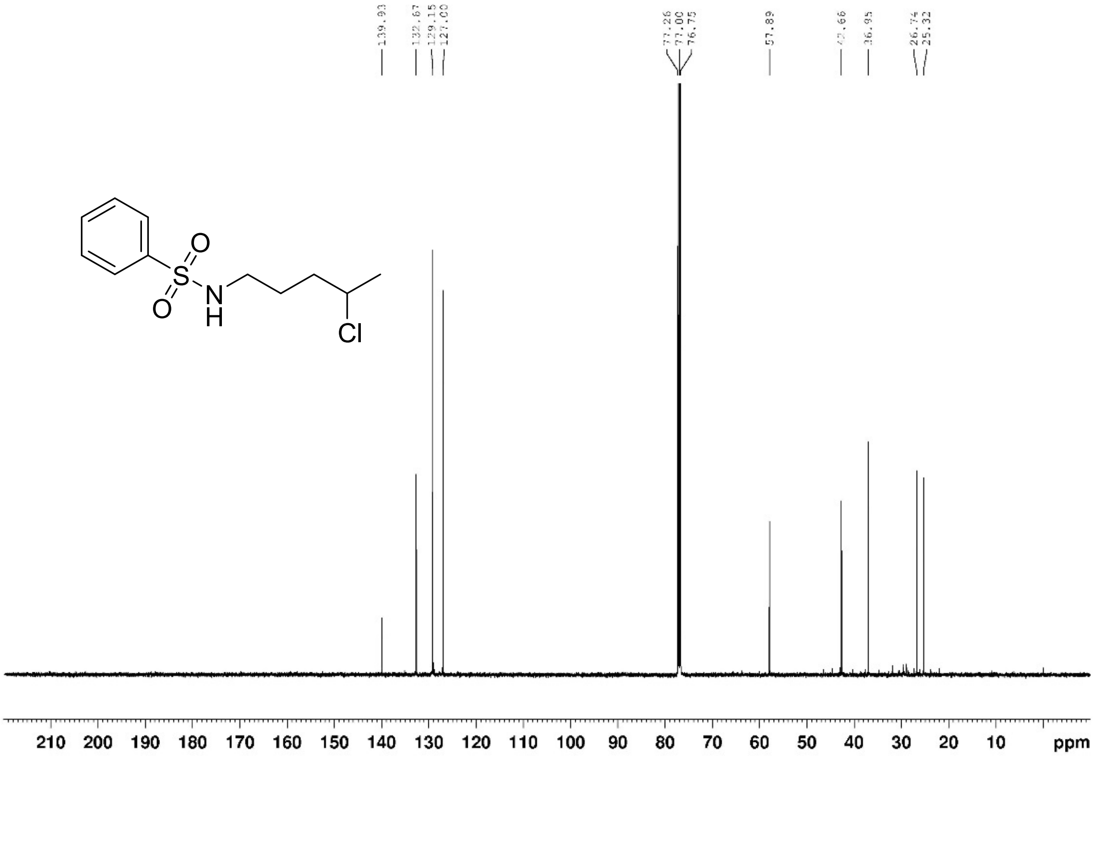
1. (a)Zhu, Y.; Shi, J.; Yu, W., Photoinduced Site-Selective C(sp3)–H Chlorination of Aliphatic Amides. *Org. Lett.* **2020,** *22*, 8899-8903; (b)Qin, Q.; Yu, S., Visible-Light-Promoted Remote C(sp3)–H Amidation and Chlorination. *Org. Lett.* **2015,** *17*, 1894-1897.
2. Wang, C.; Tan, C.; Zhu, Y.; Liu, G.; Huang, Y.; Liu, R., A Site-Selective C(sp3)-H Chlorination Boosted by an Imidazolium-Functionalized Cage in Water. *ACS Catal.* **2023,** *13*, 13896-13901.
3. Liu, R. Z.; Li, J.; Sun, J.; Liu, X. G.; Qu, S.; Li, P.; Zhang, B., Generation and Reactivity of Amidyl Radicals: Manganese-Mediated Atom-Transfer Reaction. *Angew. Chem. Int. Ed.* **2020,** *59*, 4428-4433.
4. Ji, Y.-X.; Li, J.; Li, C.-M.; Qu, S.; Zhang, B., Manganese-Catalyzed N–F Bond Activation for Hydroamination and Carboamination of Alkenes. *Org. Lett.* **2020,** *23*, 207-212.
5. Novaes, L. F. T.; Ho, J. S. K.; Mao, K.; Liu, K.; Tanwar, M.; Neurock, M.; Villemure, E.; Terrett, J. A.; Lin, S., Exploring Electrochemical C(sp3)–H Oxidation for the Late-Stage Methylation of Complex Molecules. *J. Am. Chem. Soc.* **2022,** *144*, 1187-1197.

11. Copies of ^{1}H NMR ， ^{13}C{^{1}H} NMR and ^{19}F NMR spectra of the substrates and products

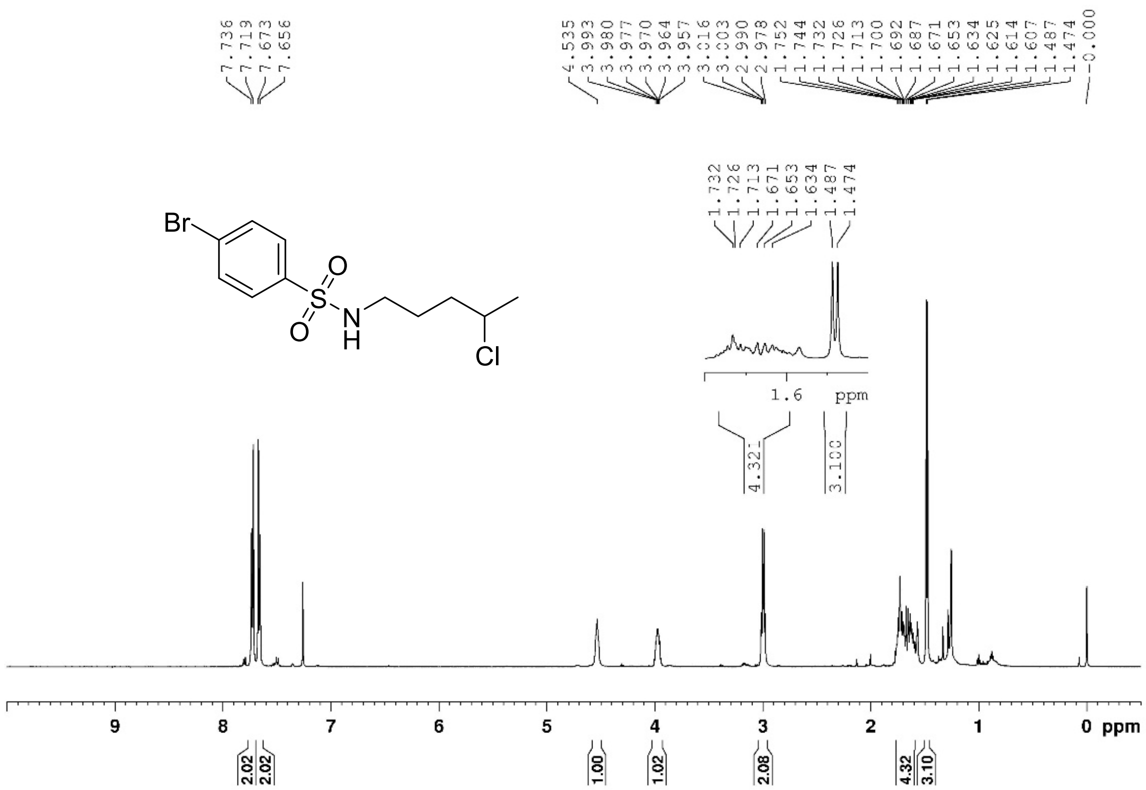
2a ^{1}H NMR (500 MHz, $CDCl_3$)



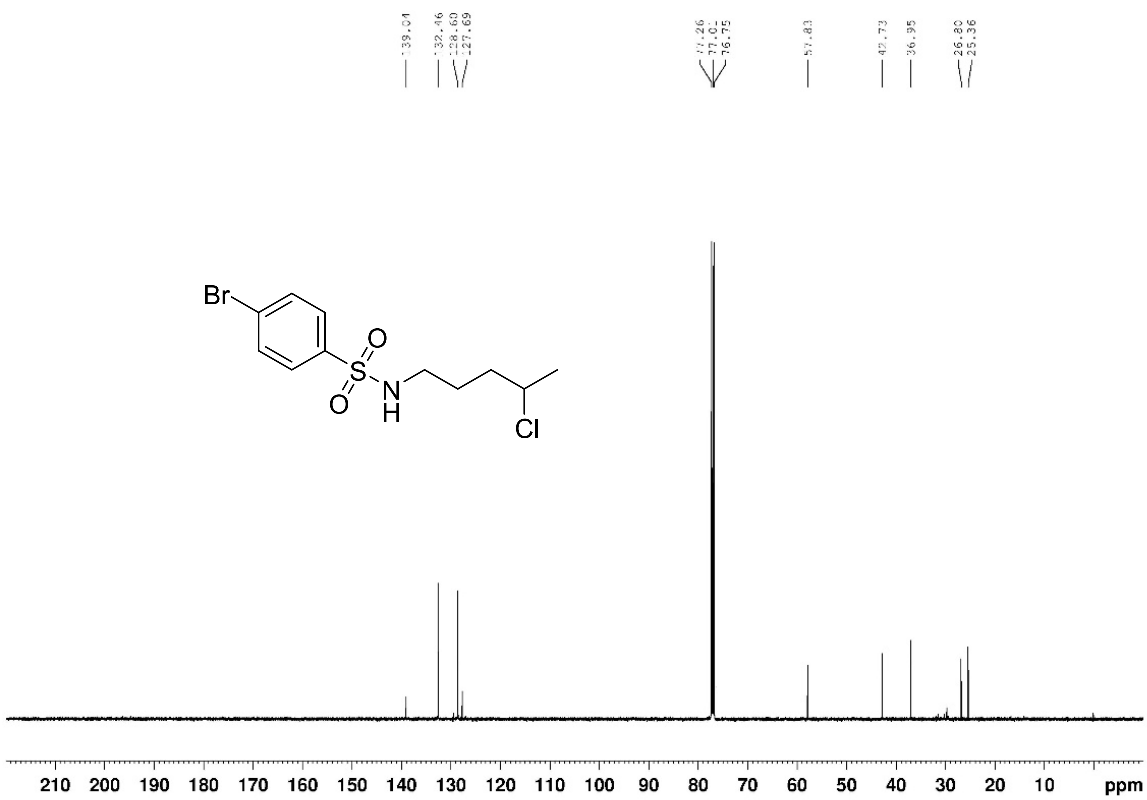
2a ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



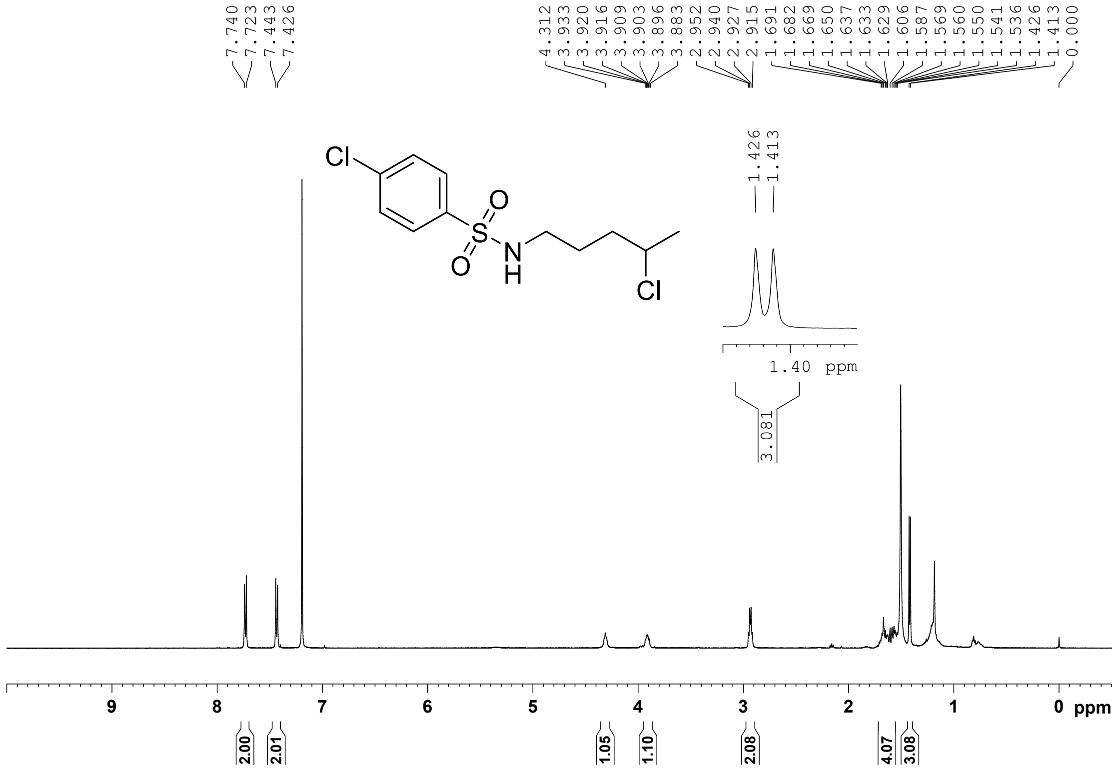
2b ^{1}H NMR (500 MHz, $CDCl_3$)



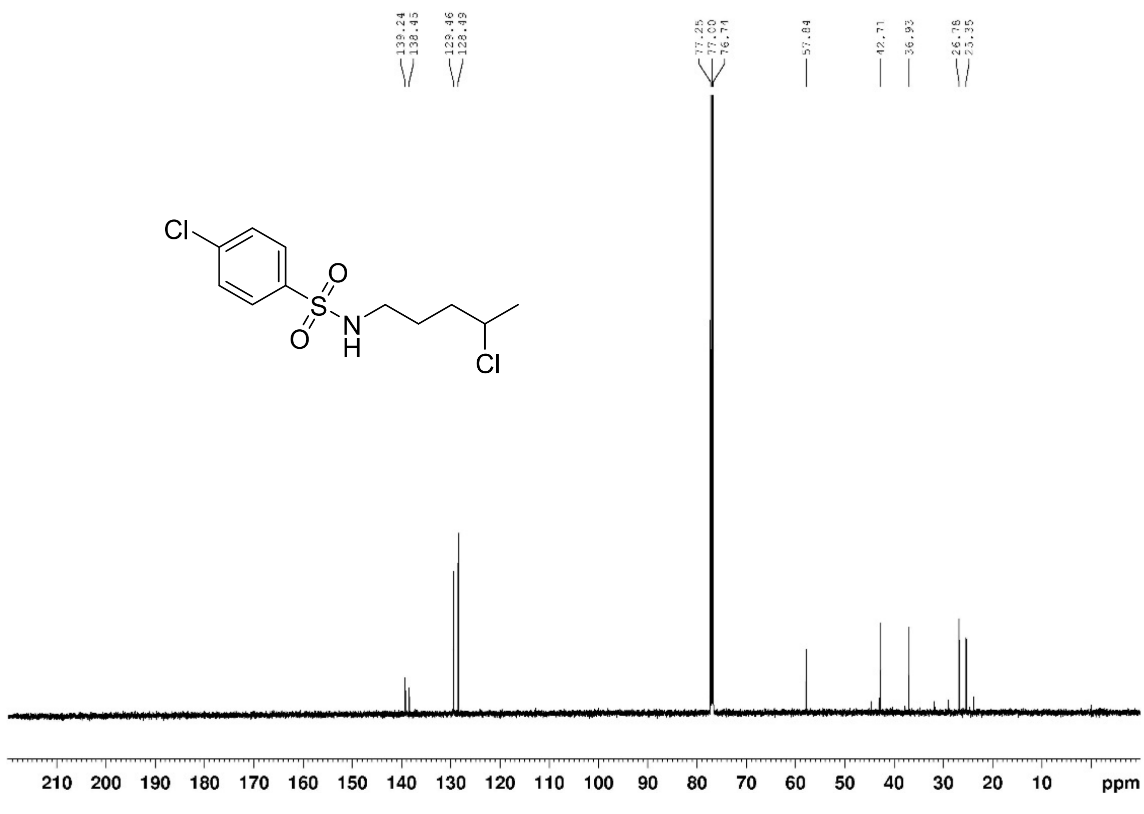
2b ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



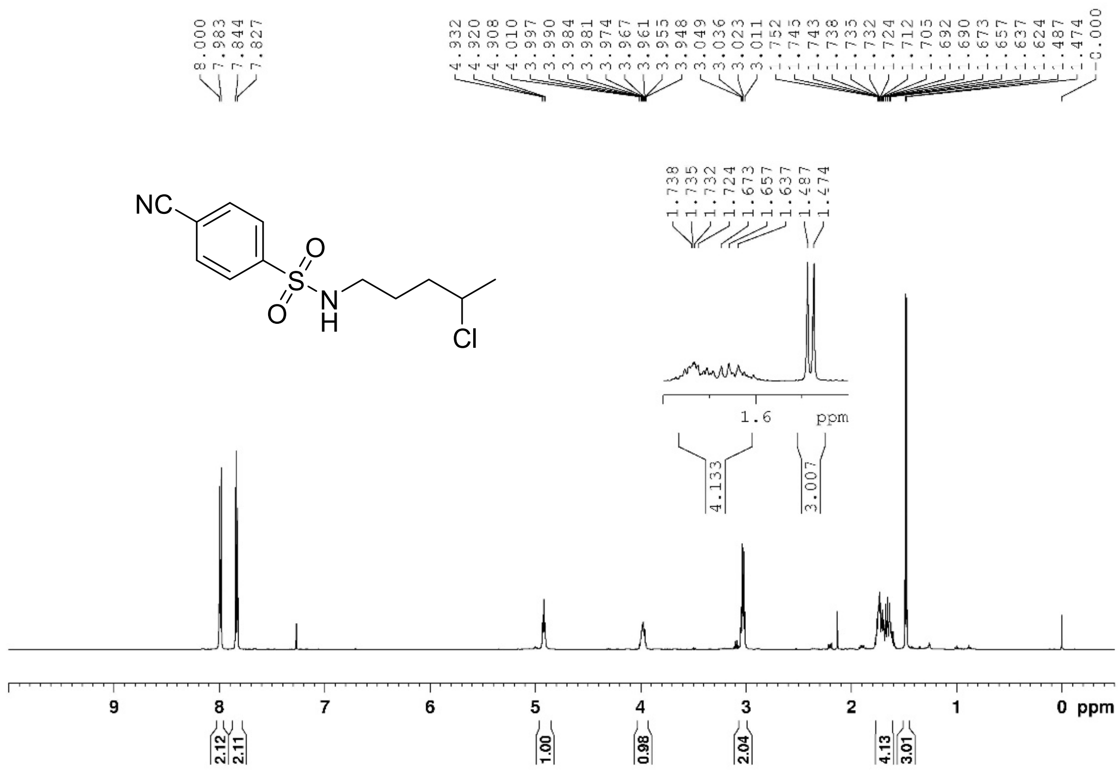
2c ^{1}H NMR (500 MHz, $CDCl_3$)



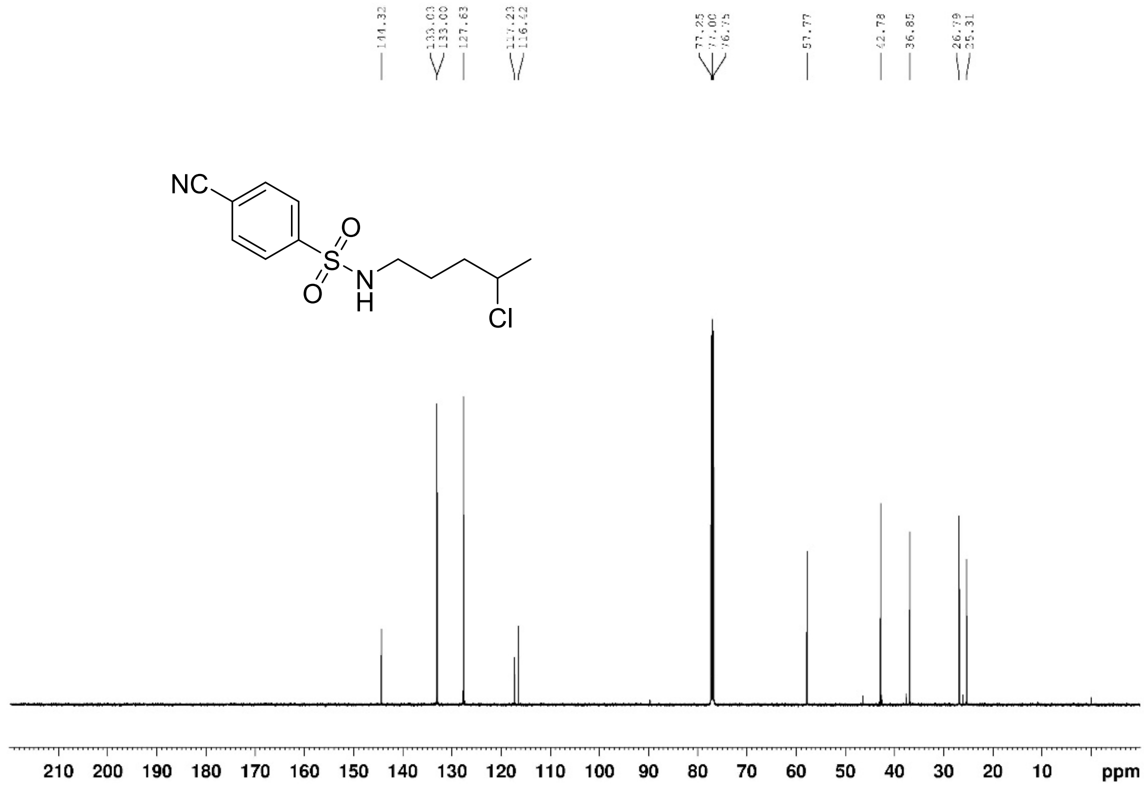
2c $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



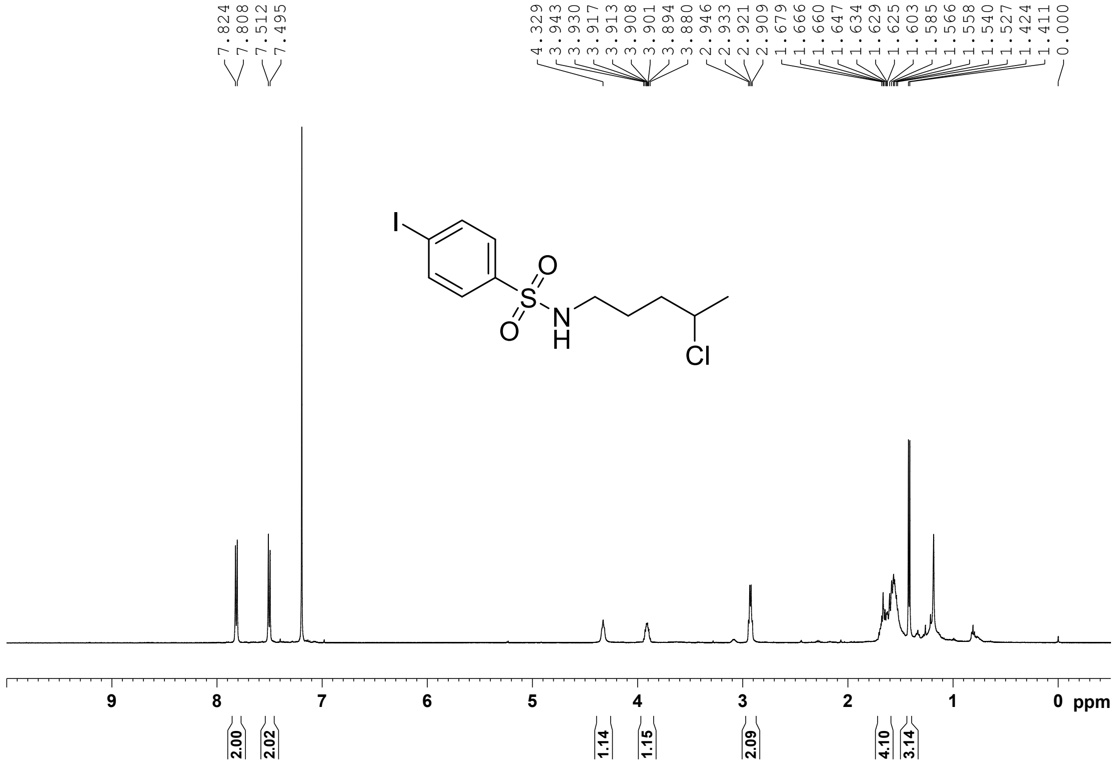
2d ^{1}H NMR (500 MHz, $CDCl_3$)



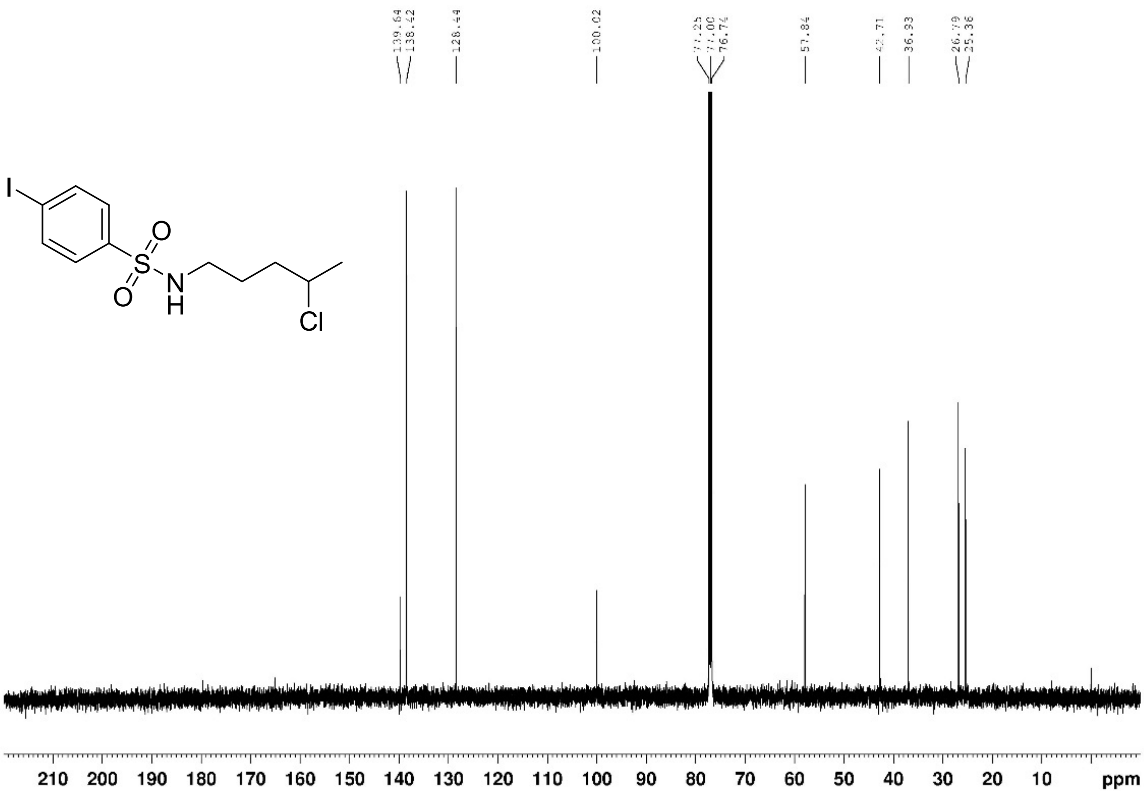
2d $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)



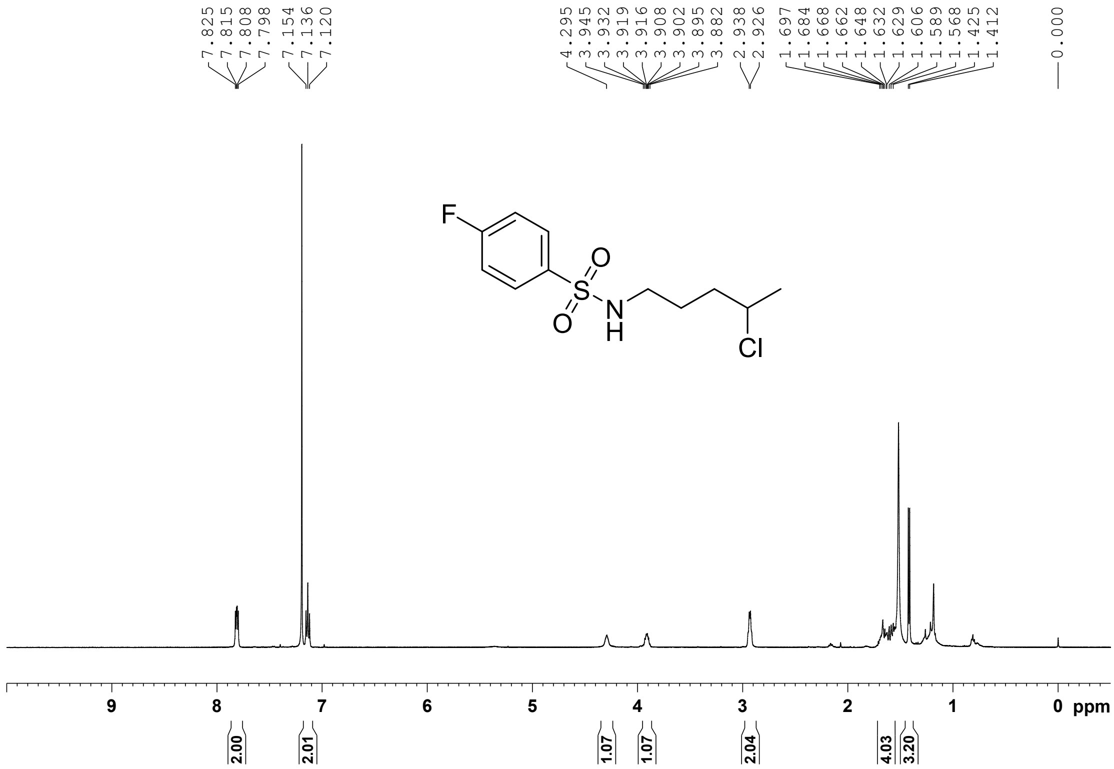
2e ^{1}H NMR (500 MHz, $CDCl_3$)



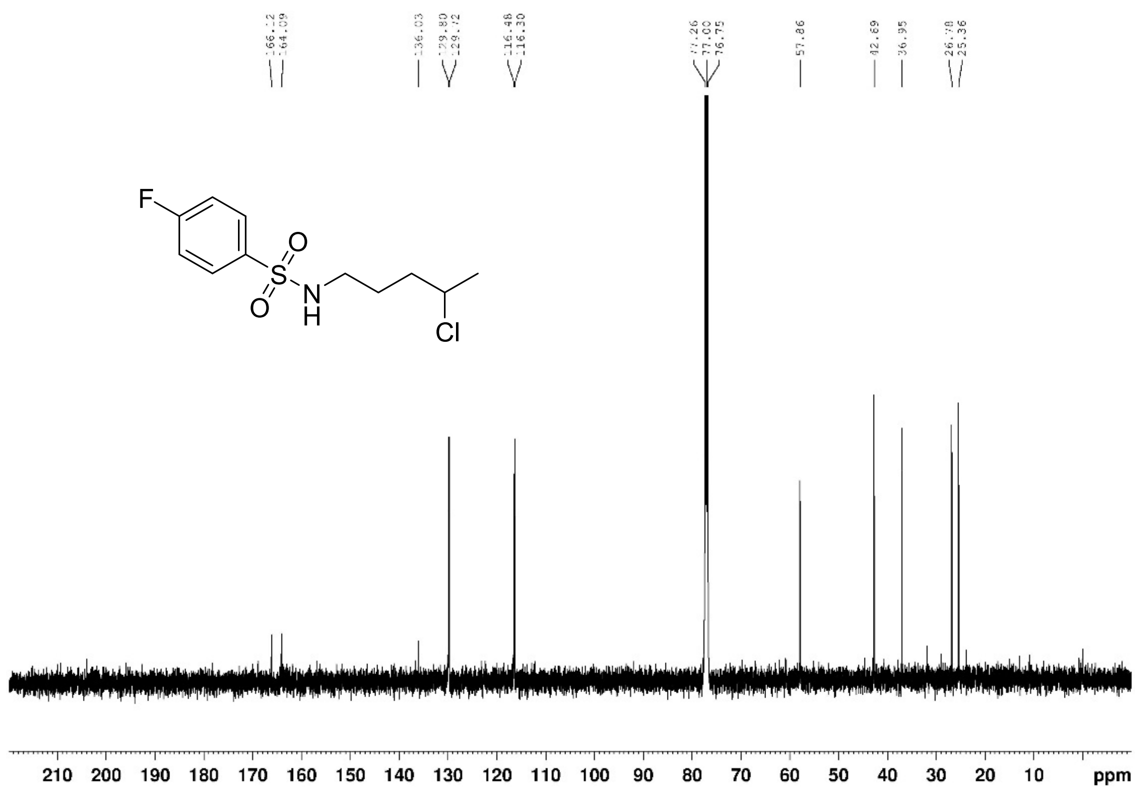
2e ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



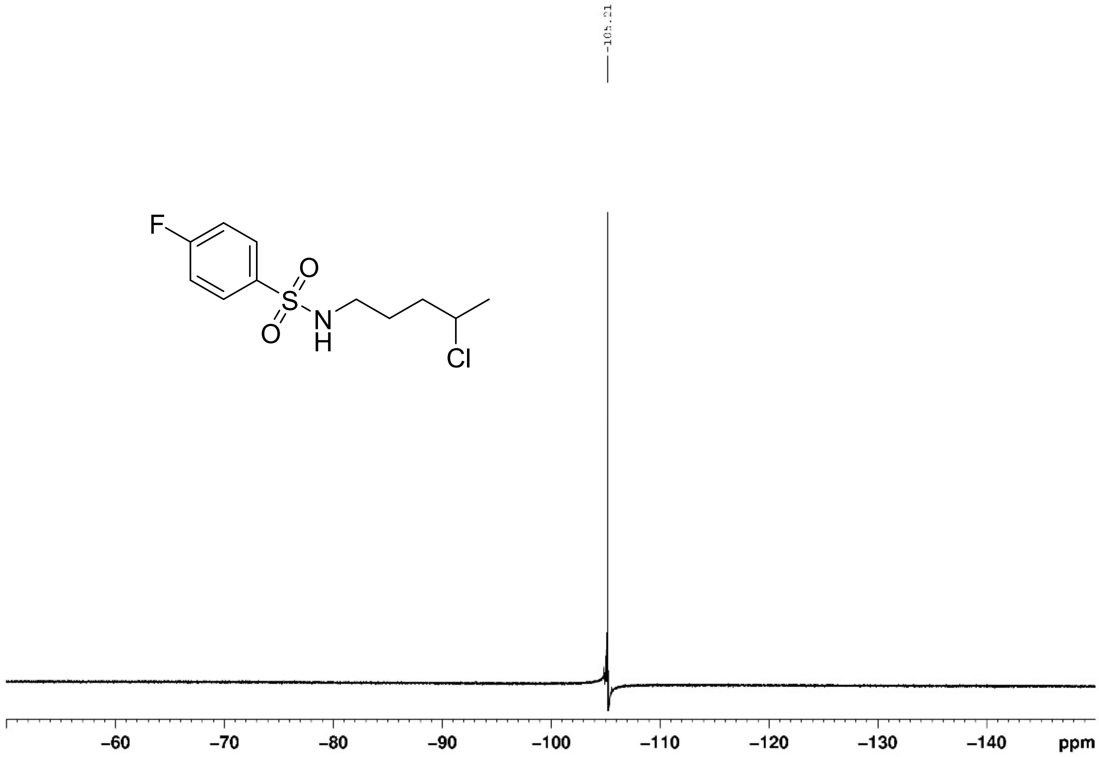
2f ^{1}H NMR (500 MHz, $CDCl_3$)



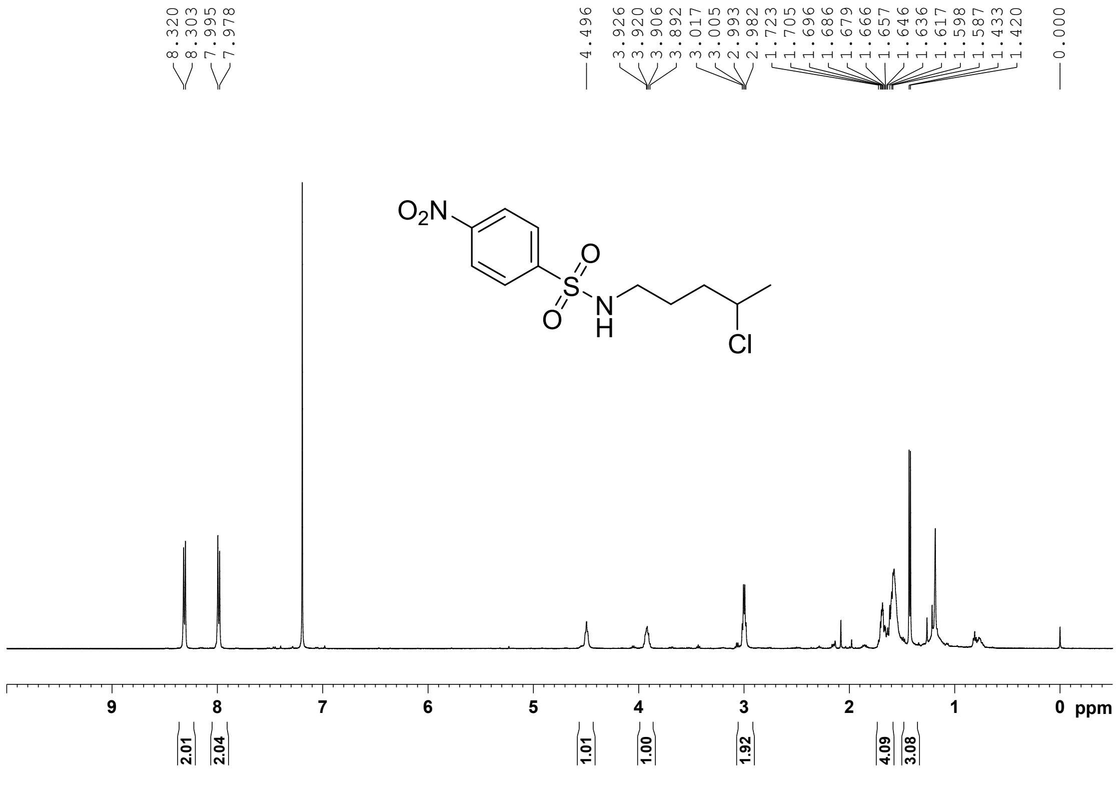
2f $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



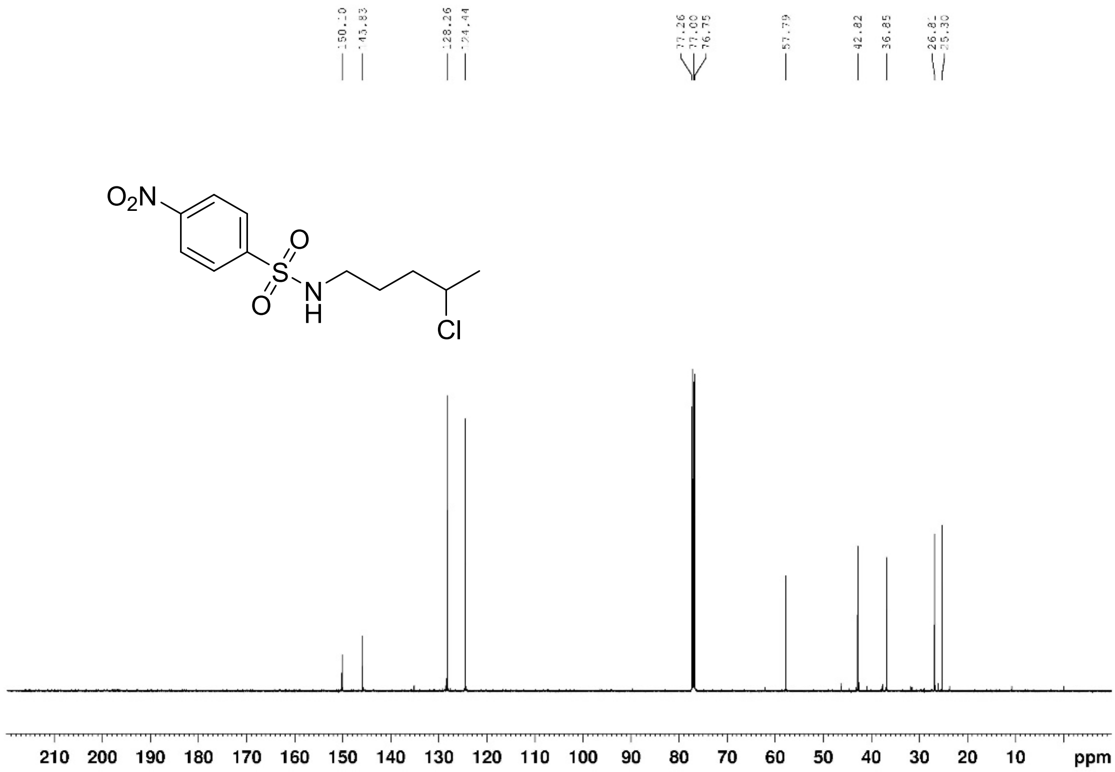
2e ^{19}F NMR (471 MHz, $CDCl_3$)



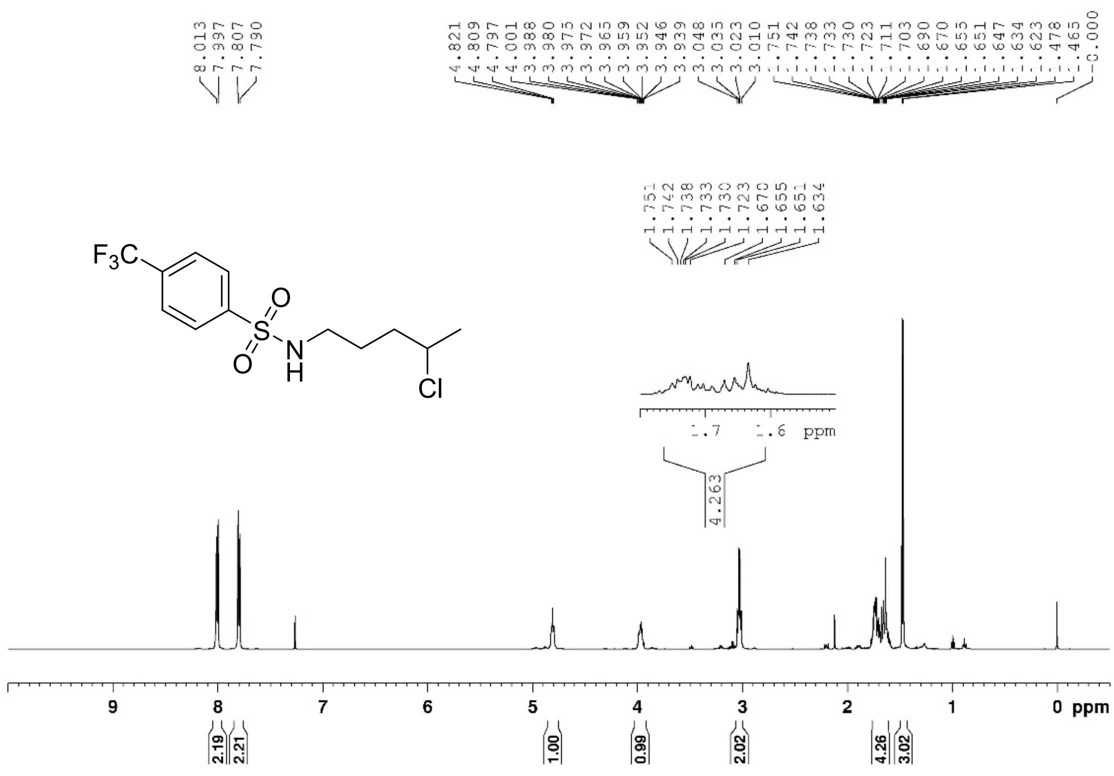
2g ^{1}H NMR (500 MHz, $CDCl_3$)



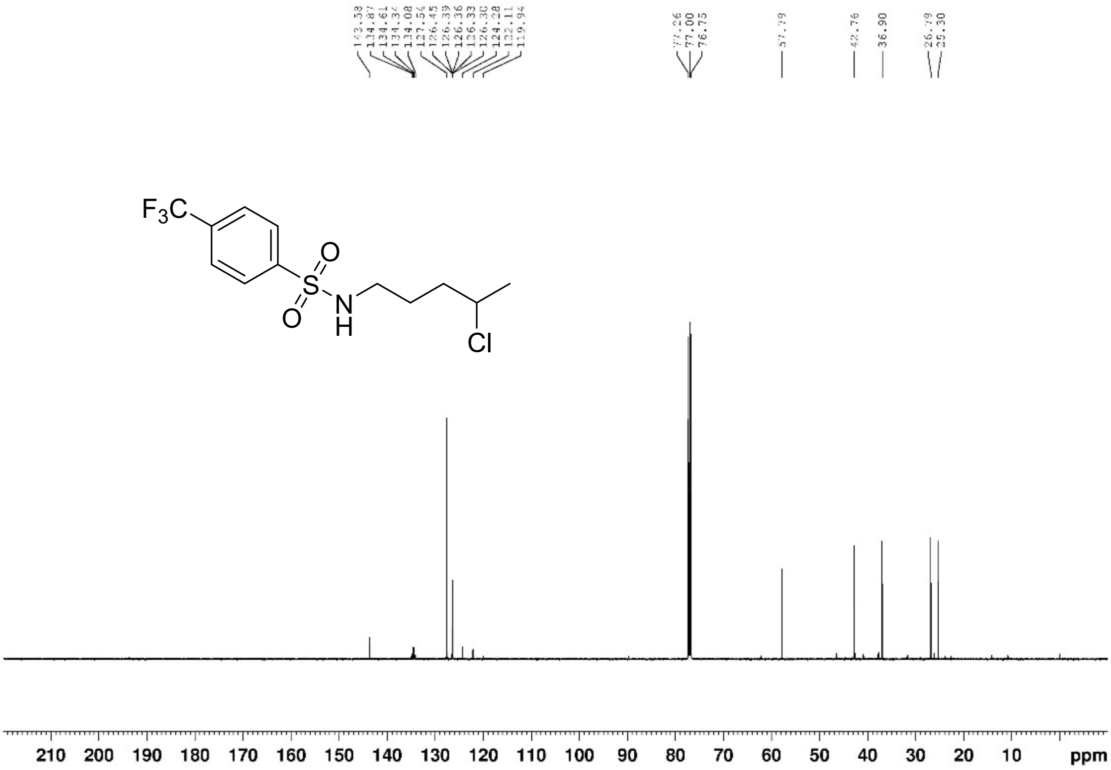
2g $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



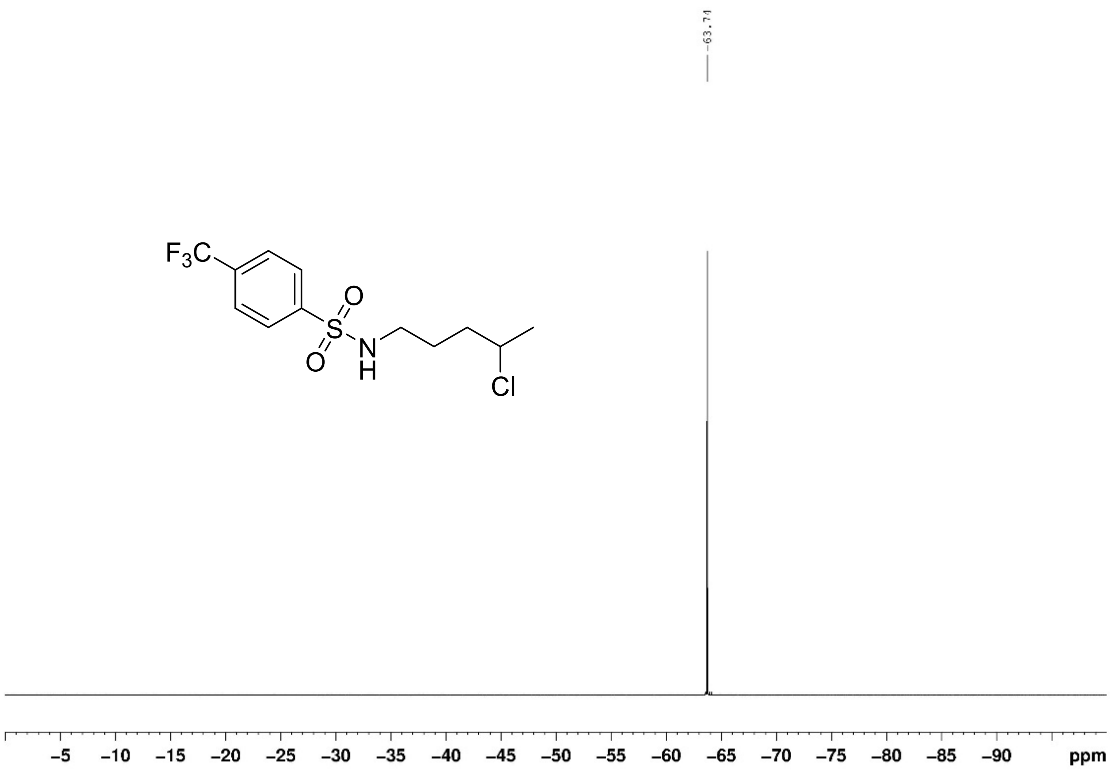
2h ^{1}H NMR (500 MHz, $CDCl_3$)



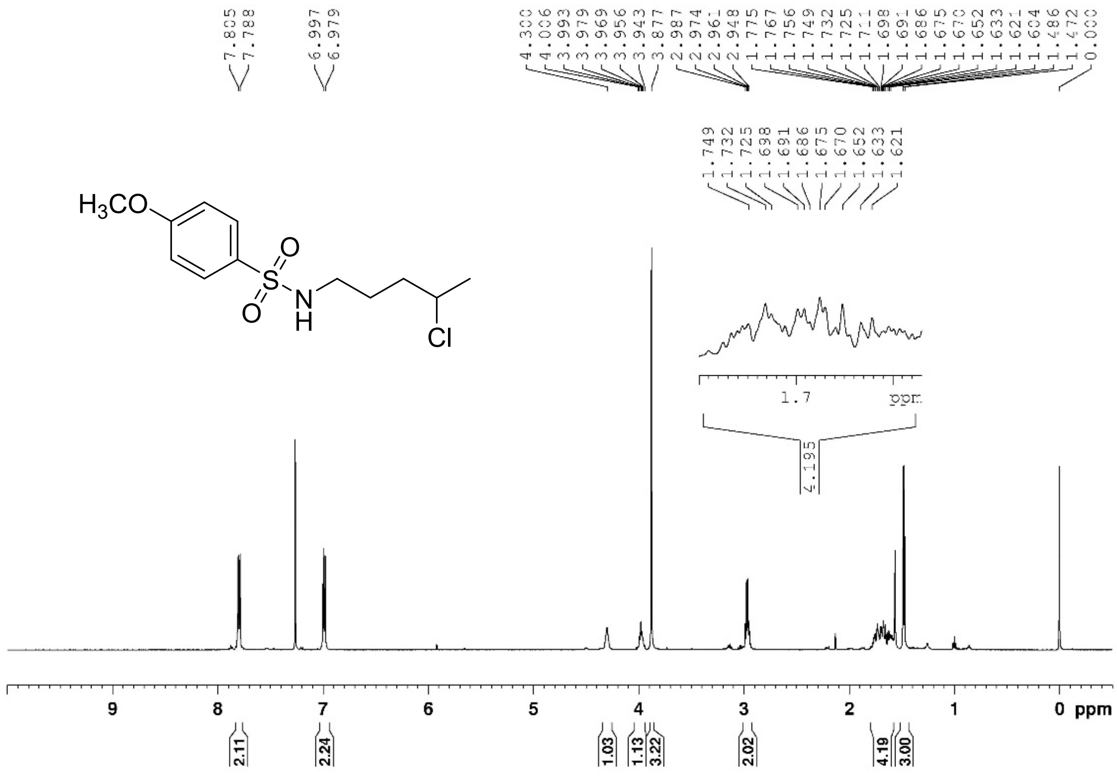
2h $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



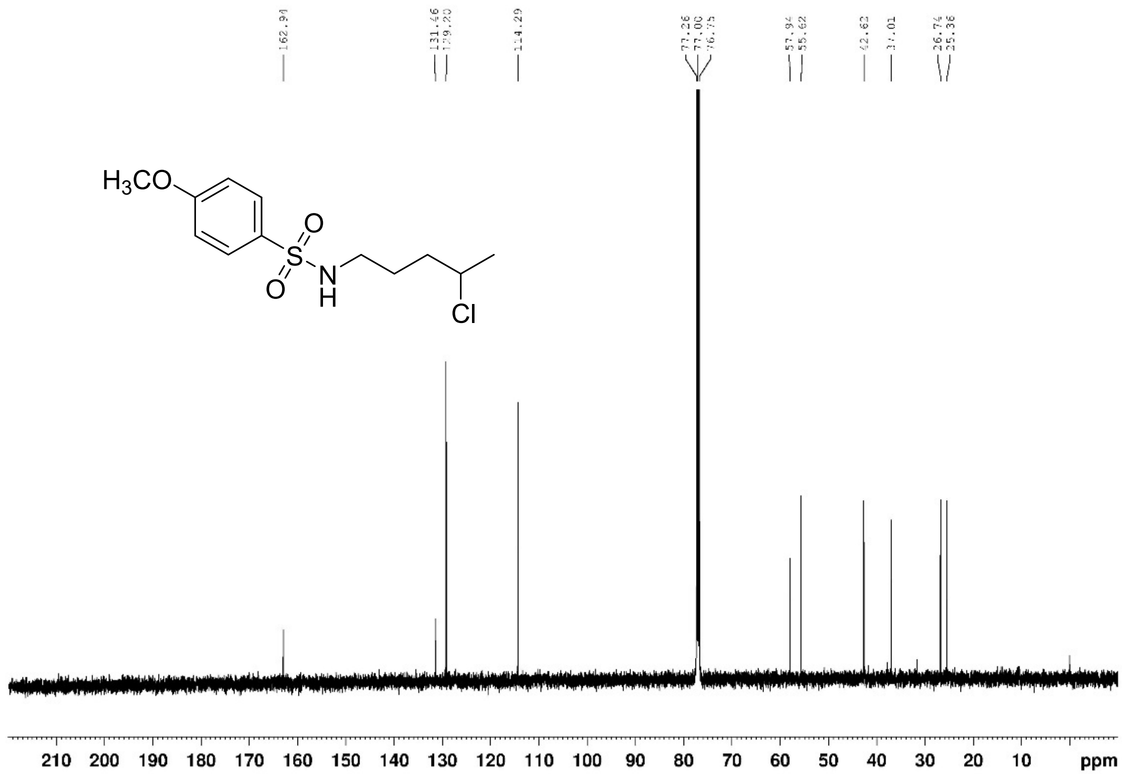
2h ^{19}F NMR (471 MHz, $CDCl_3$)



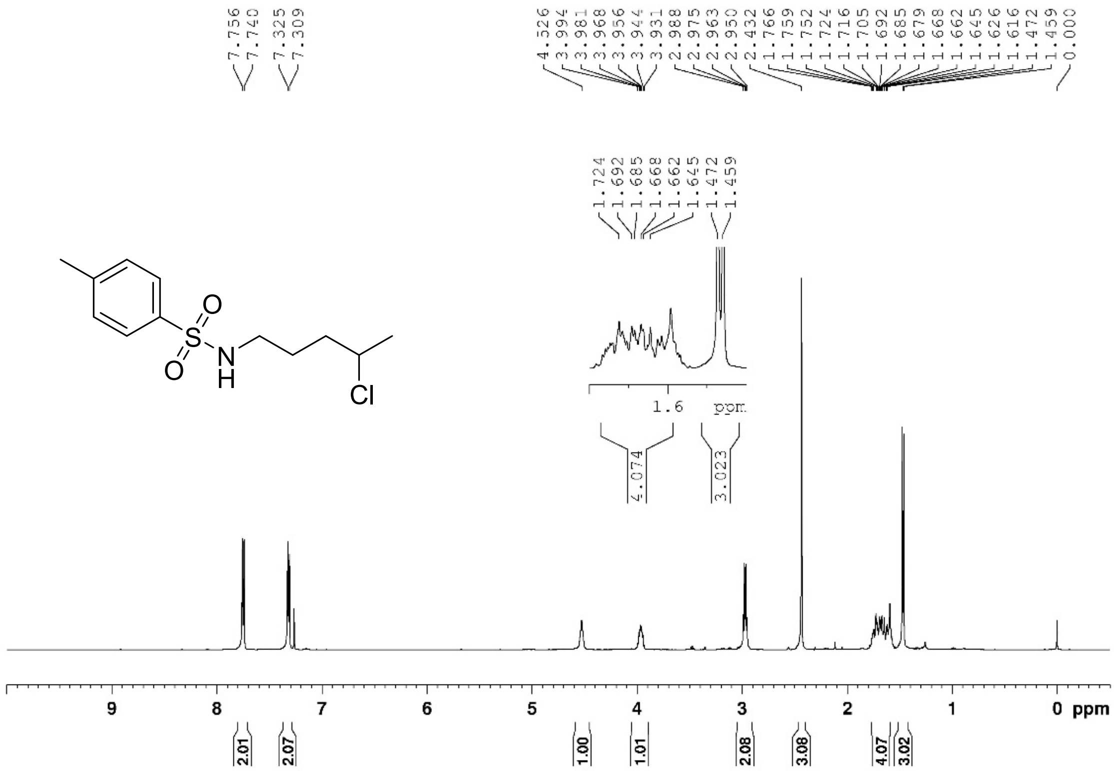
2i ^{1}H NMR (500 MHz, CDCl$_3$)



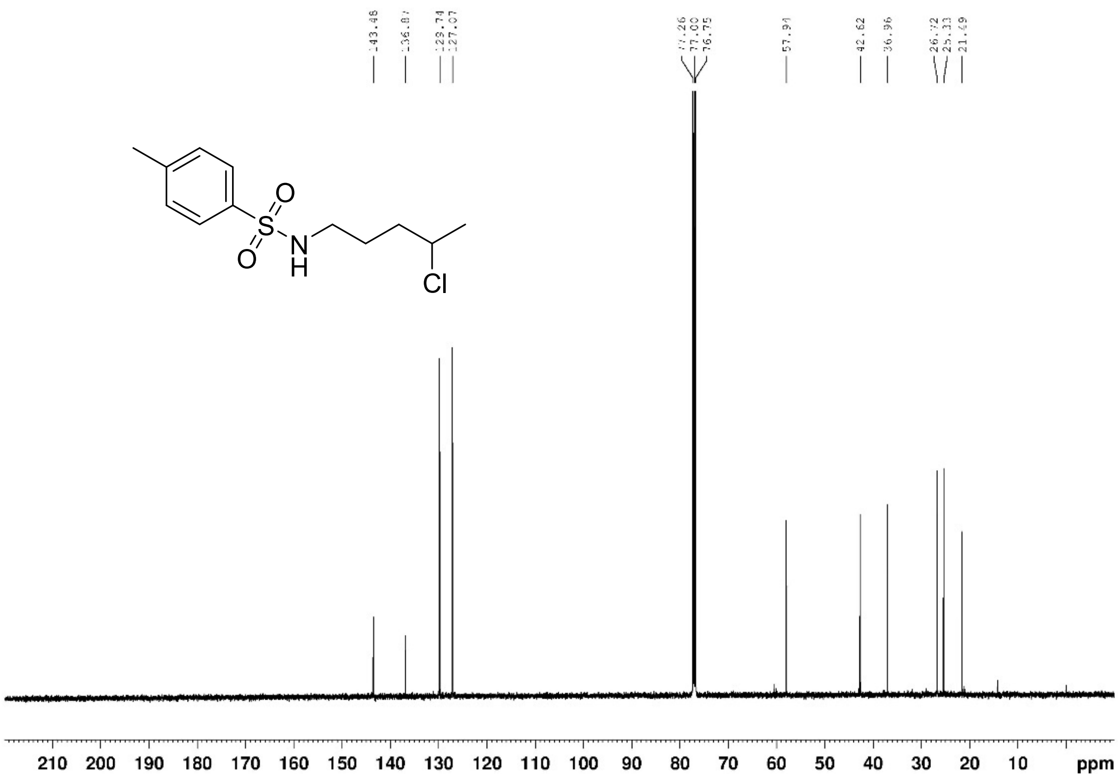
2i ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)



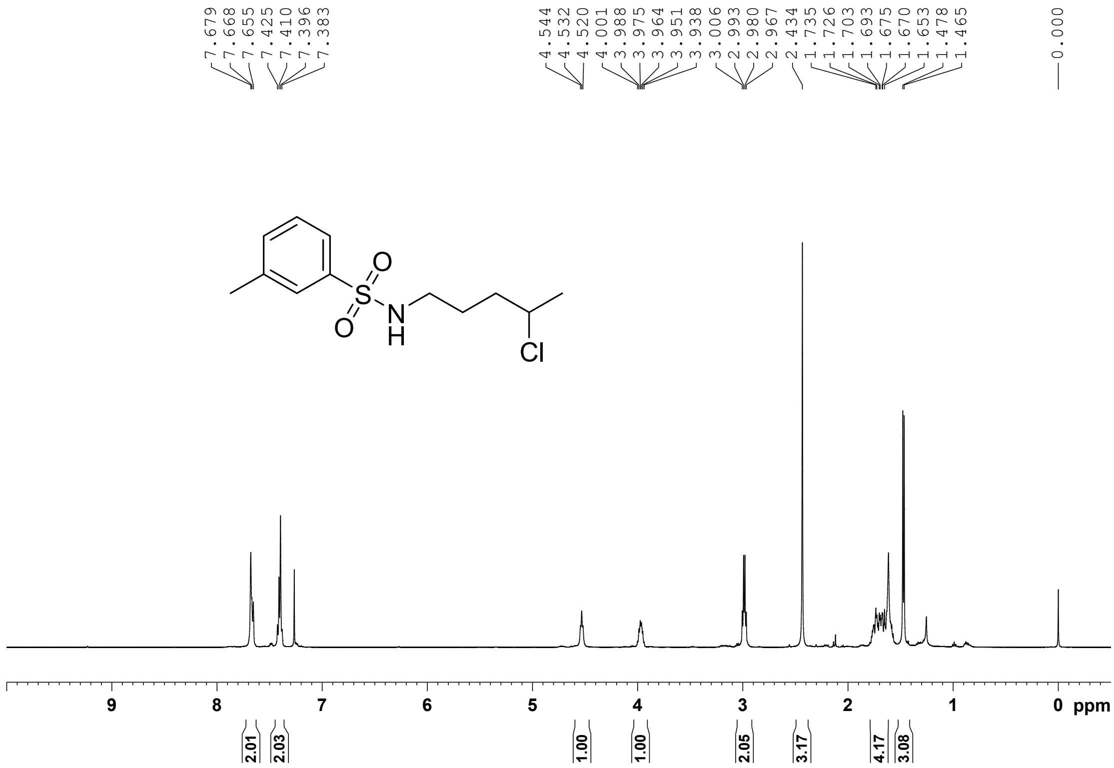
2j ¹H NMR (500 MHz, $CDCl_3$)



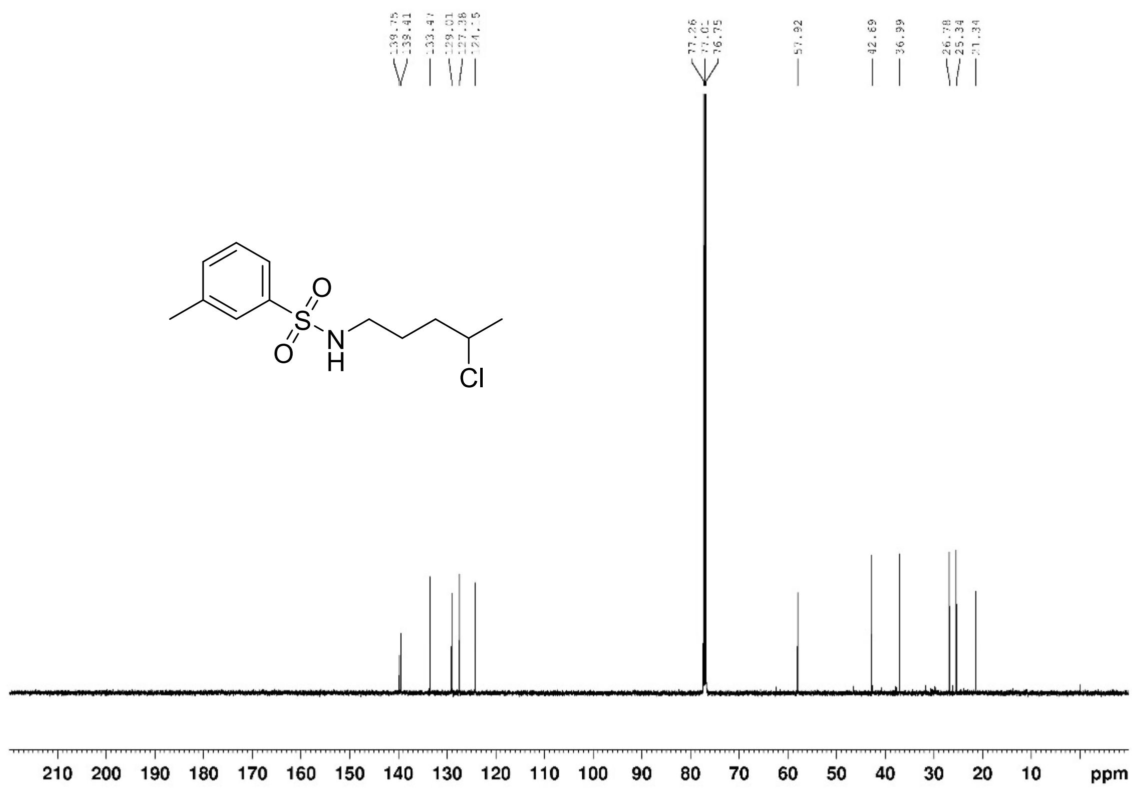
2j $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)



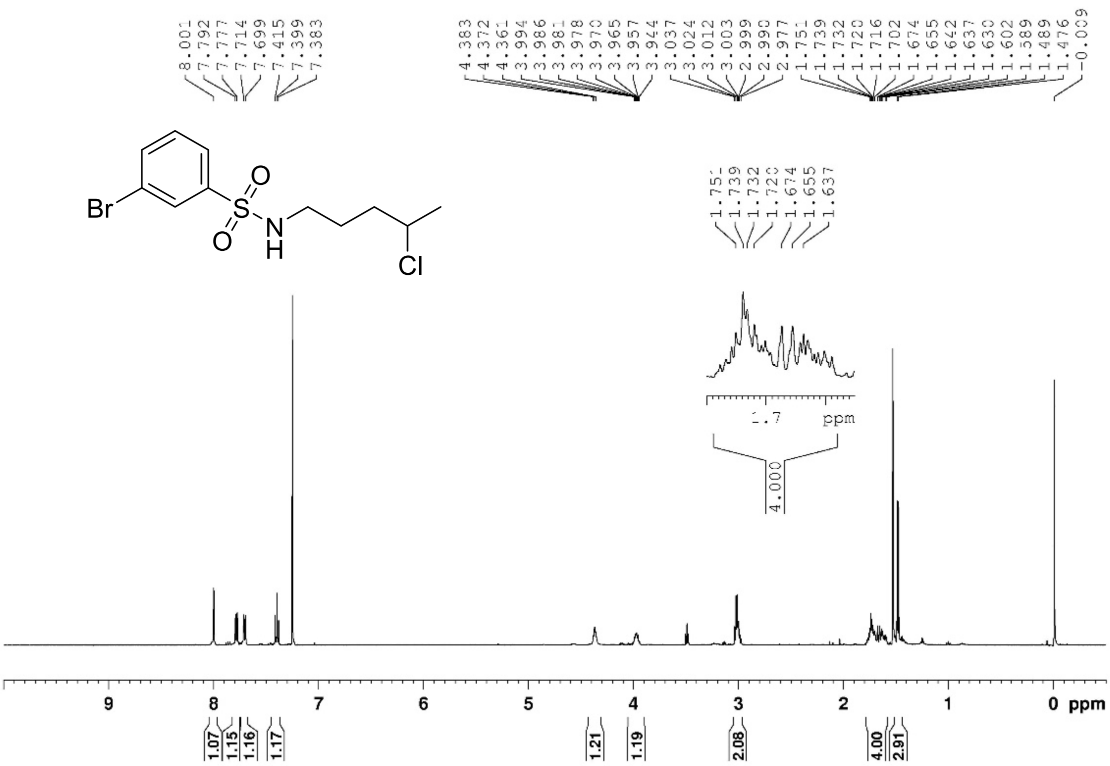
2k ^{1}H NMR (500 MHz, $CDCl_3$)



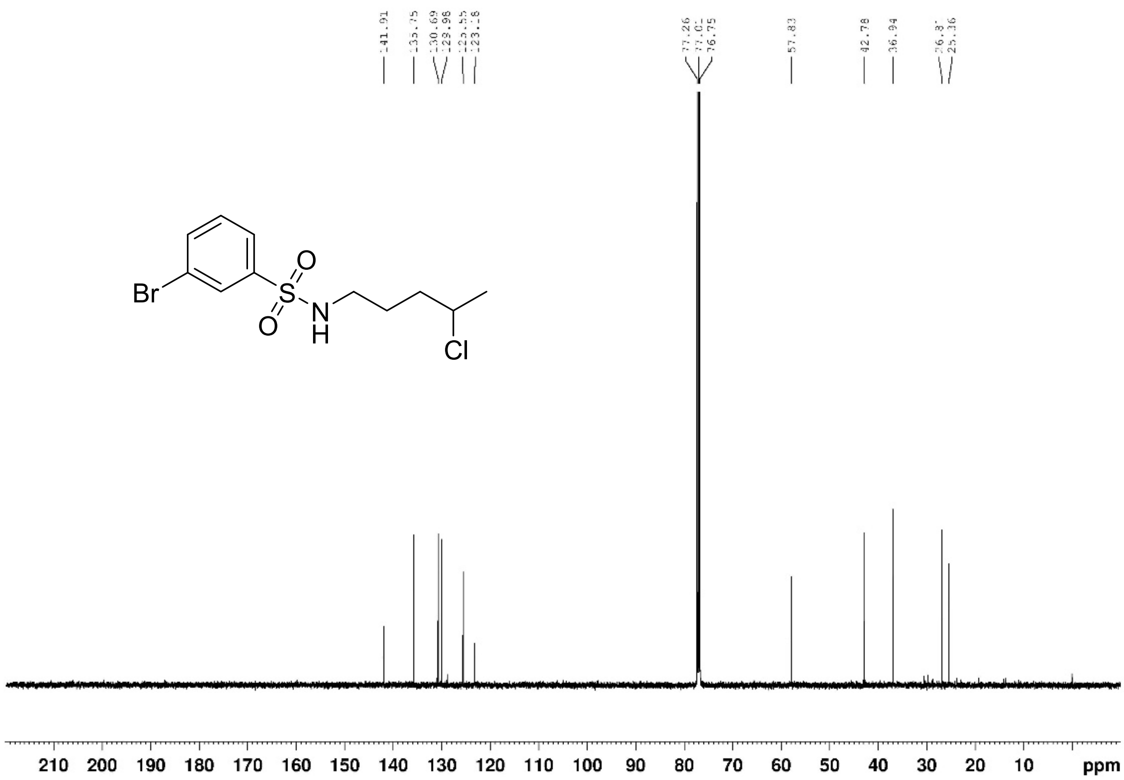
2k $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



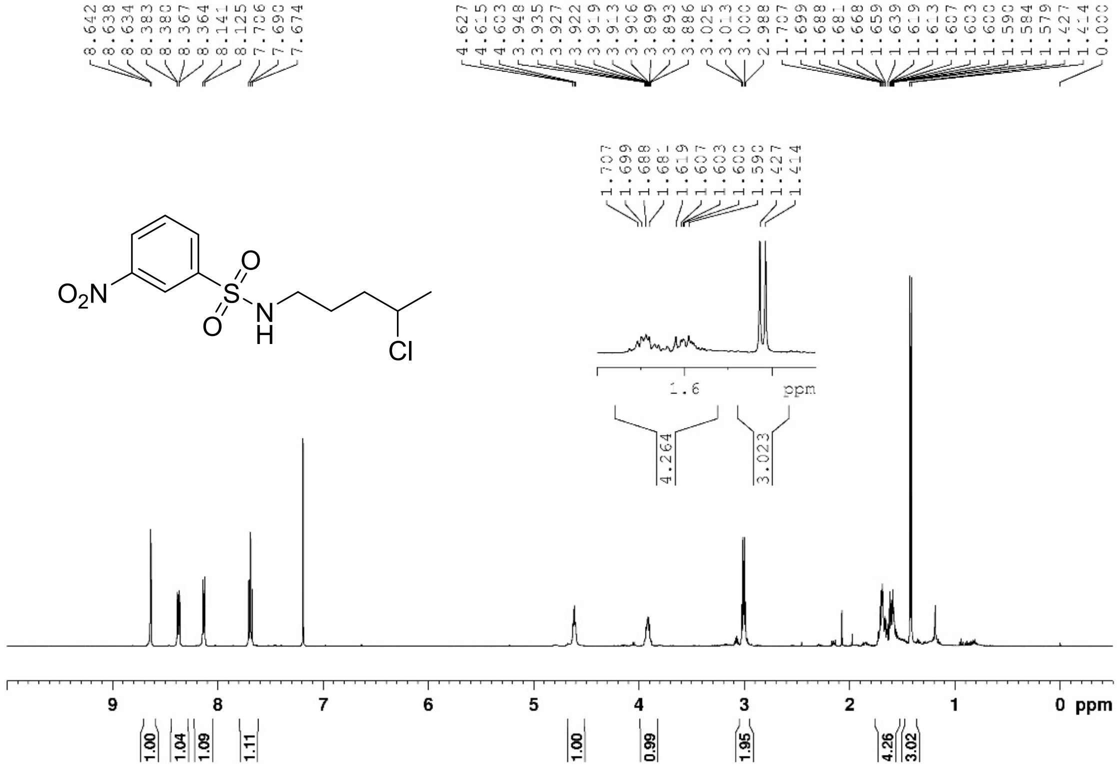
2l ^{1}H NMR (500 MHz, $CDCl_3$)



2l $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)

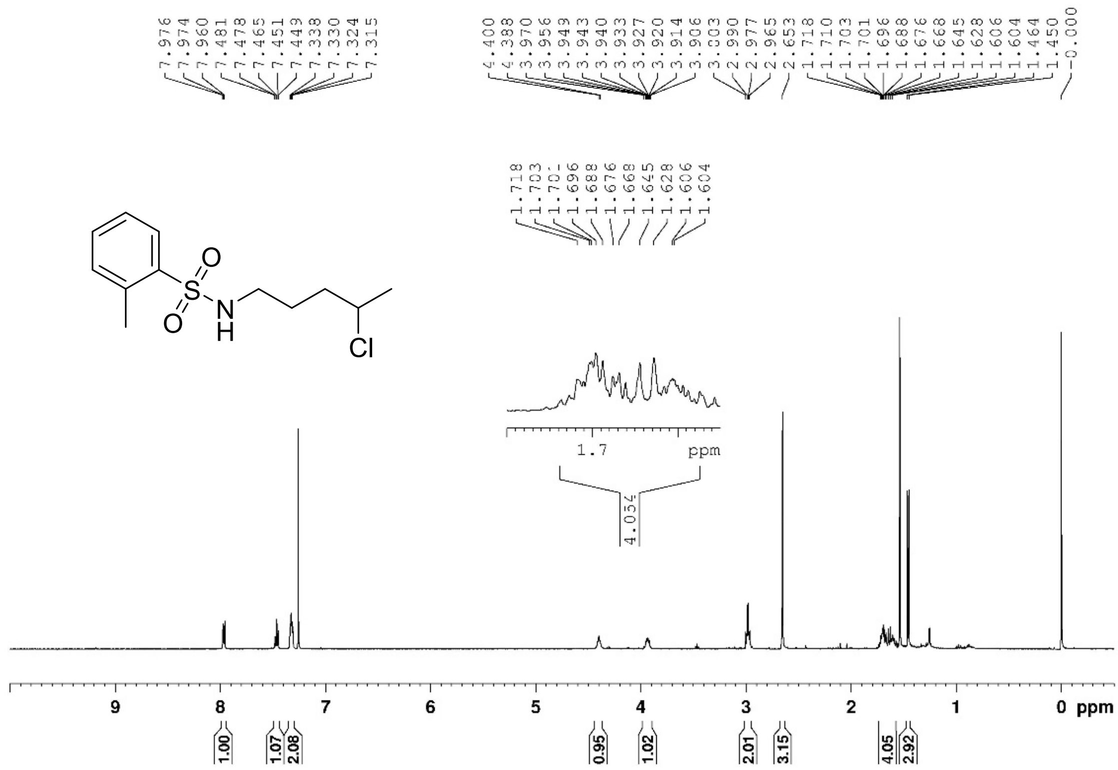


2m ^{1}H NMR (500 MHz, $CDCl_3$)

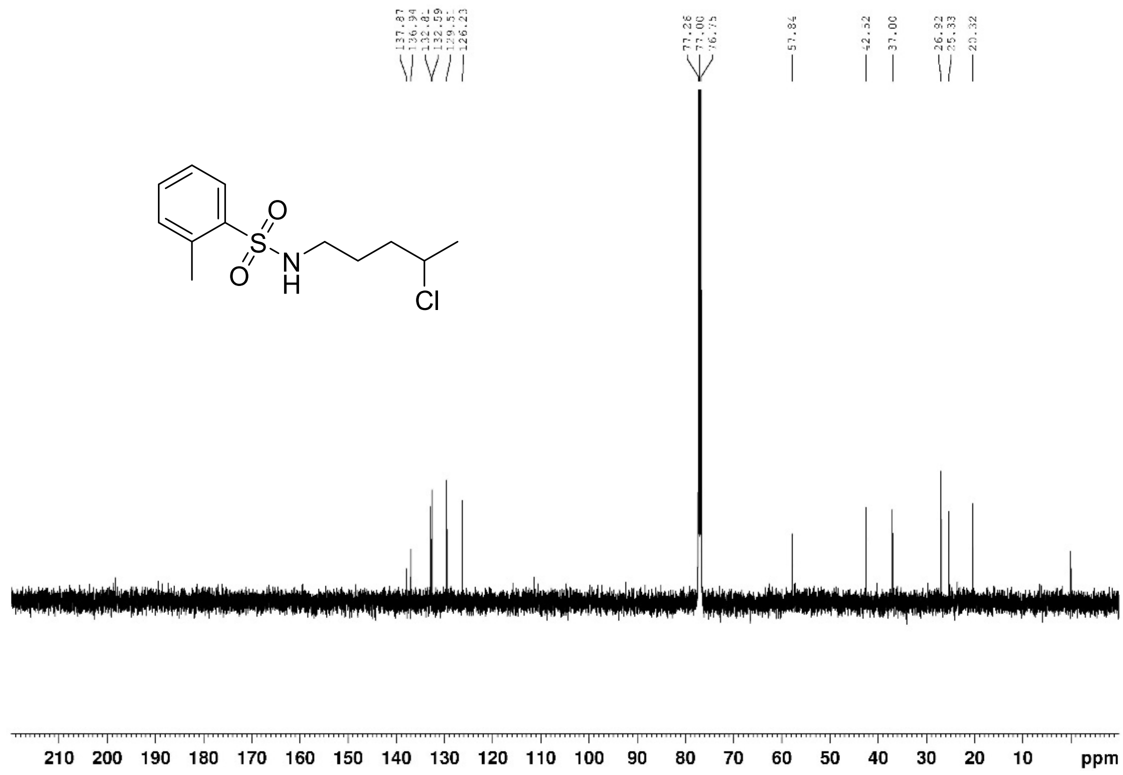


2m $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)

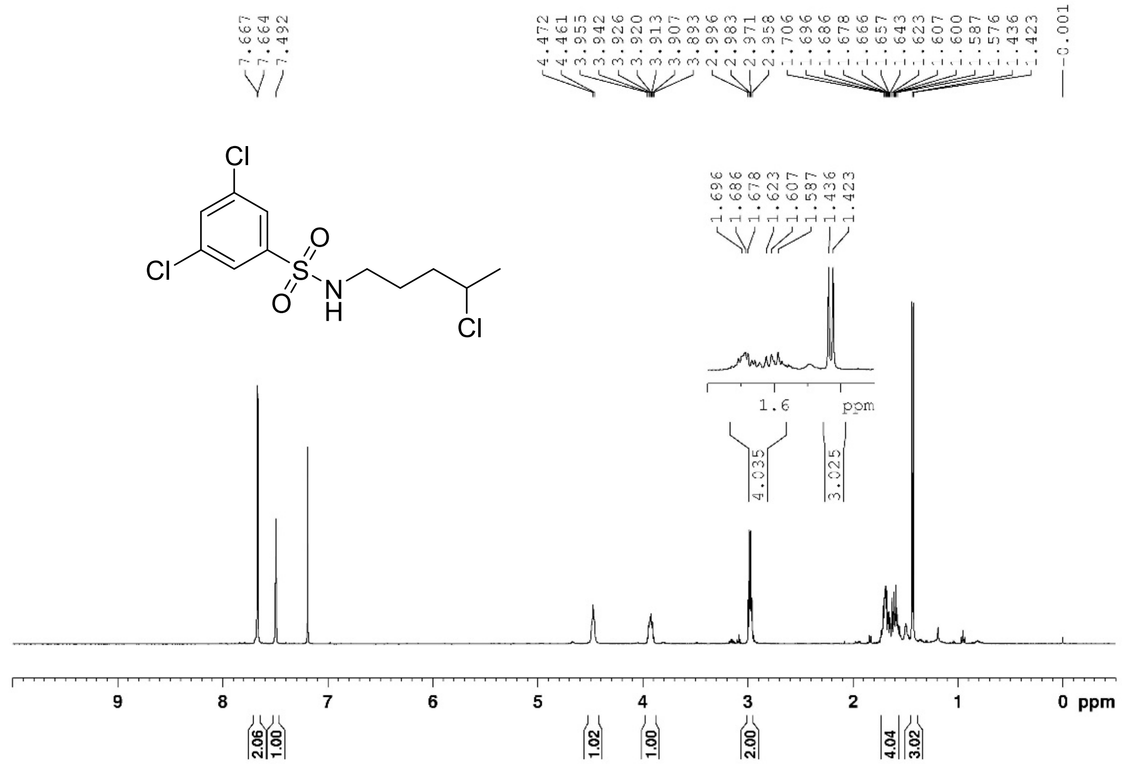
2n ^{1}H NMR (500 MHz, $CDCl_3$)



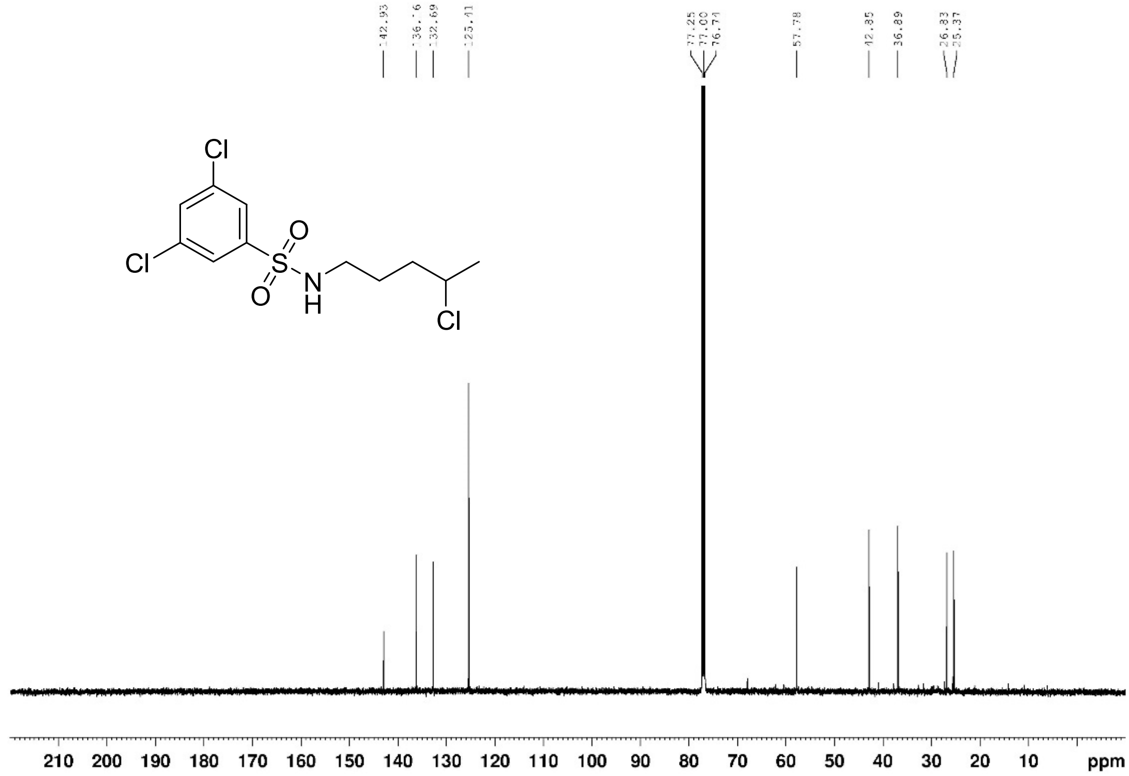
2n $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



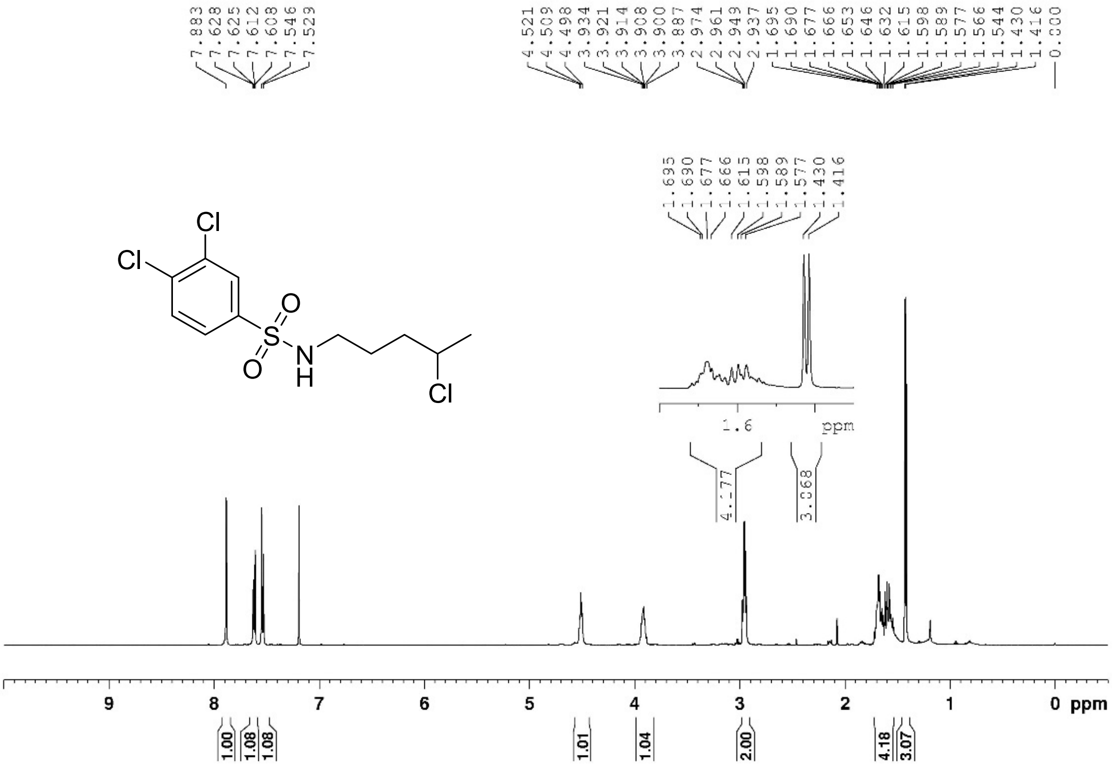
2p ^{1}H NMR (500 MHz, CDCl$_3$)



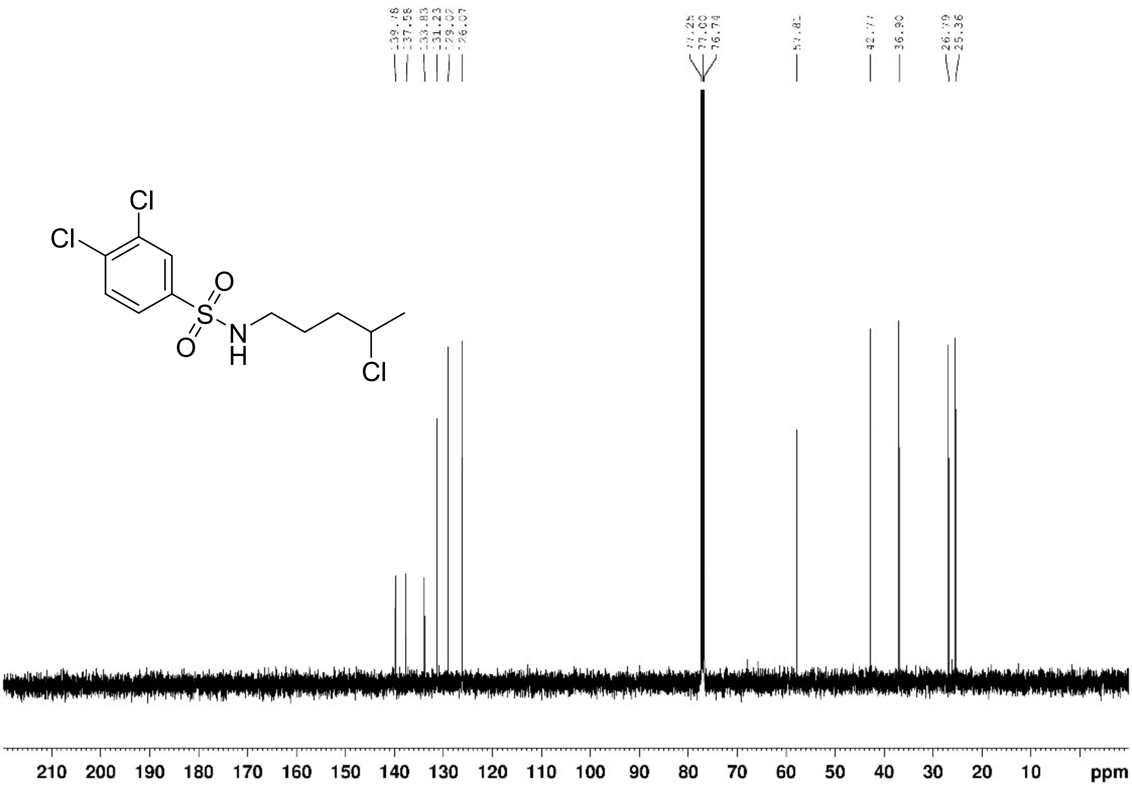
2p ^{13}C{^{1}H} NMR (126 MHz, CDCl$_3$)



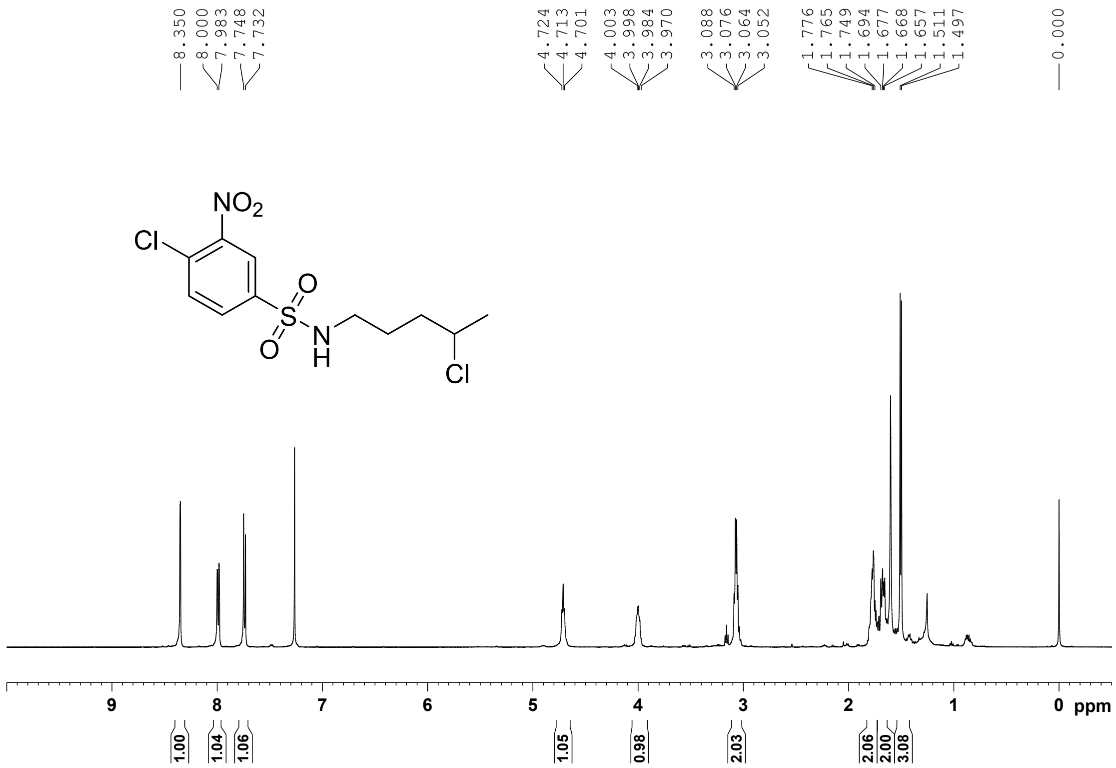
2q ^{1}H NMR (500 MHz, $CDCl_3$)



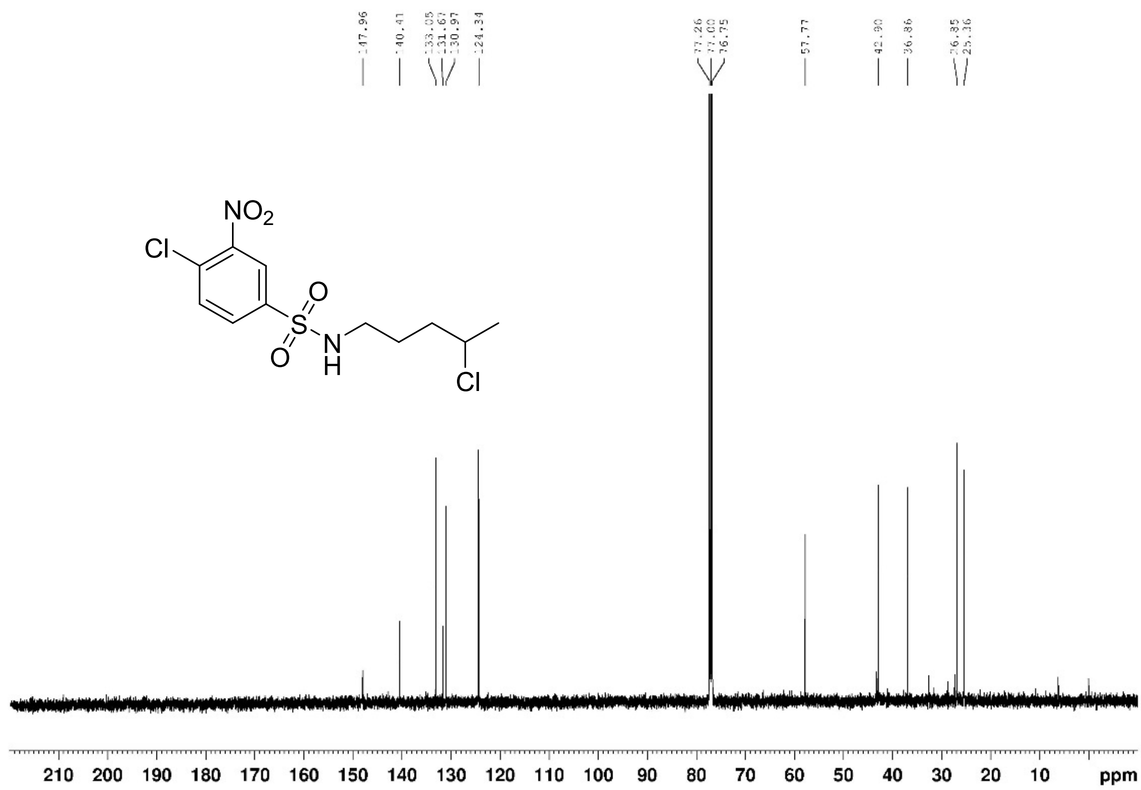
2q $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



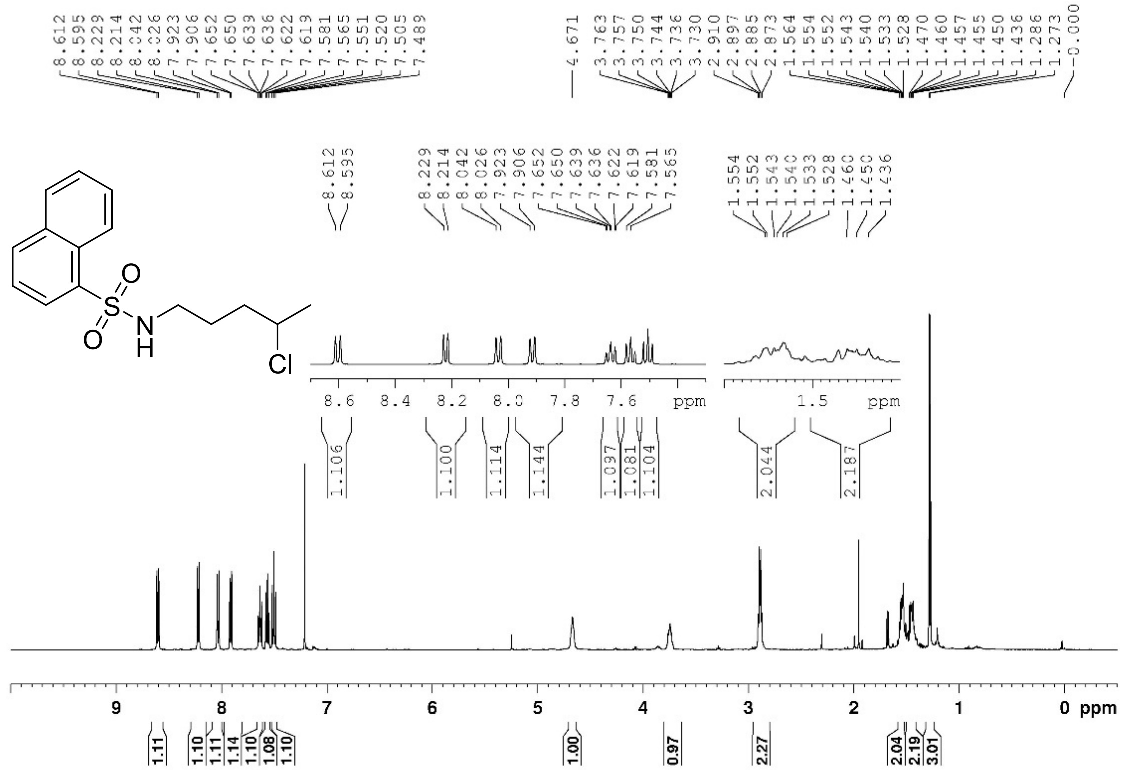
2r ^{1}H NMR (500 MHz, $CDCl_3$)



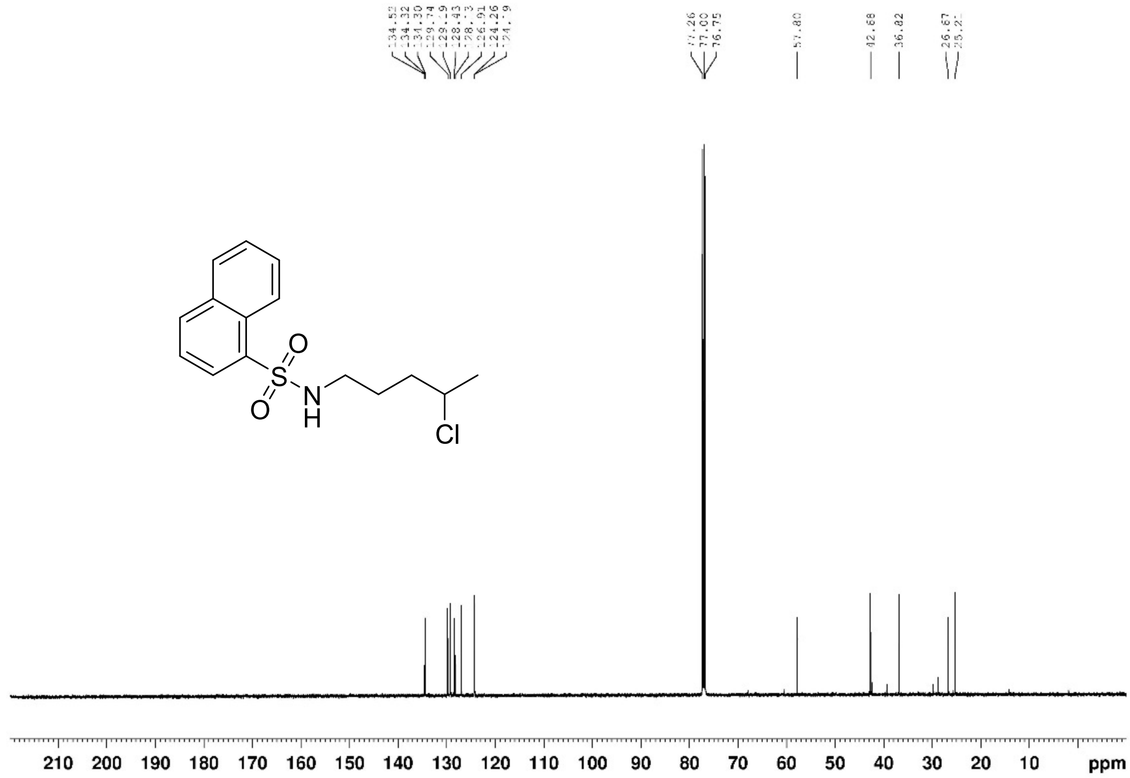
2r ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



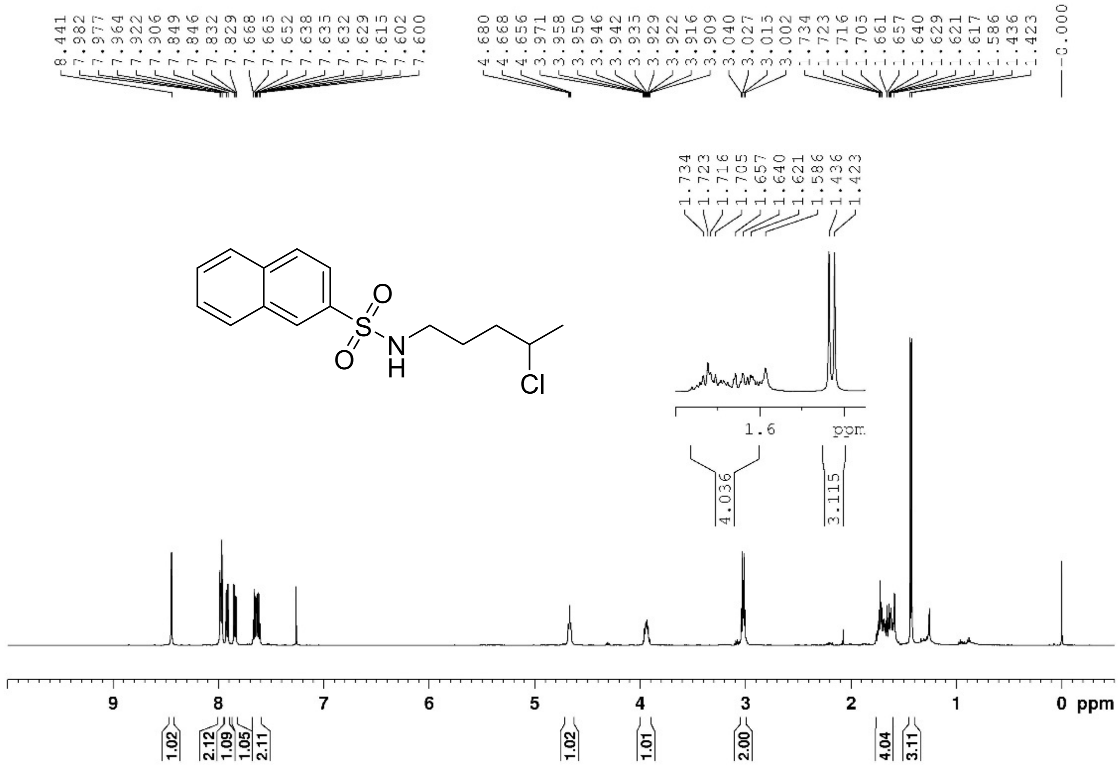
2s ^{1}H NMR (500 MHz, $CDCl_3$)



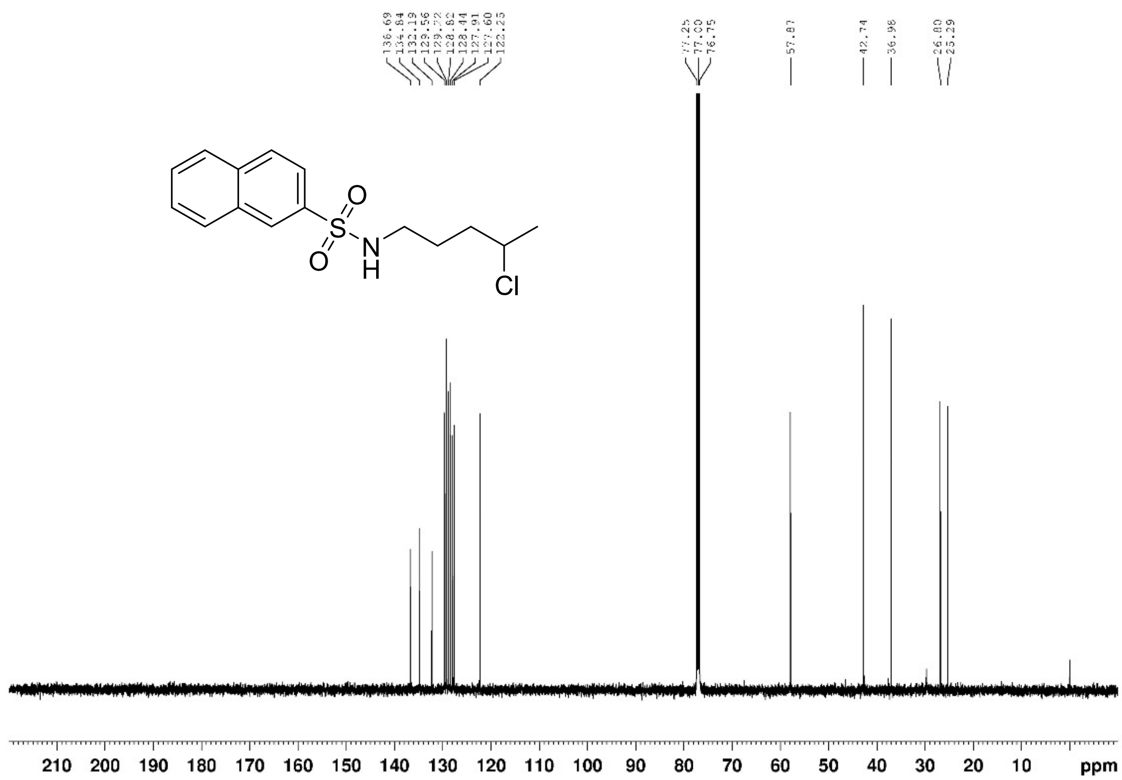
2s ^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$)



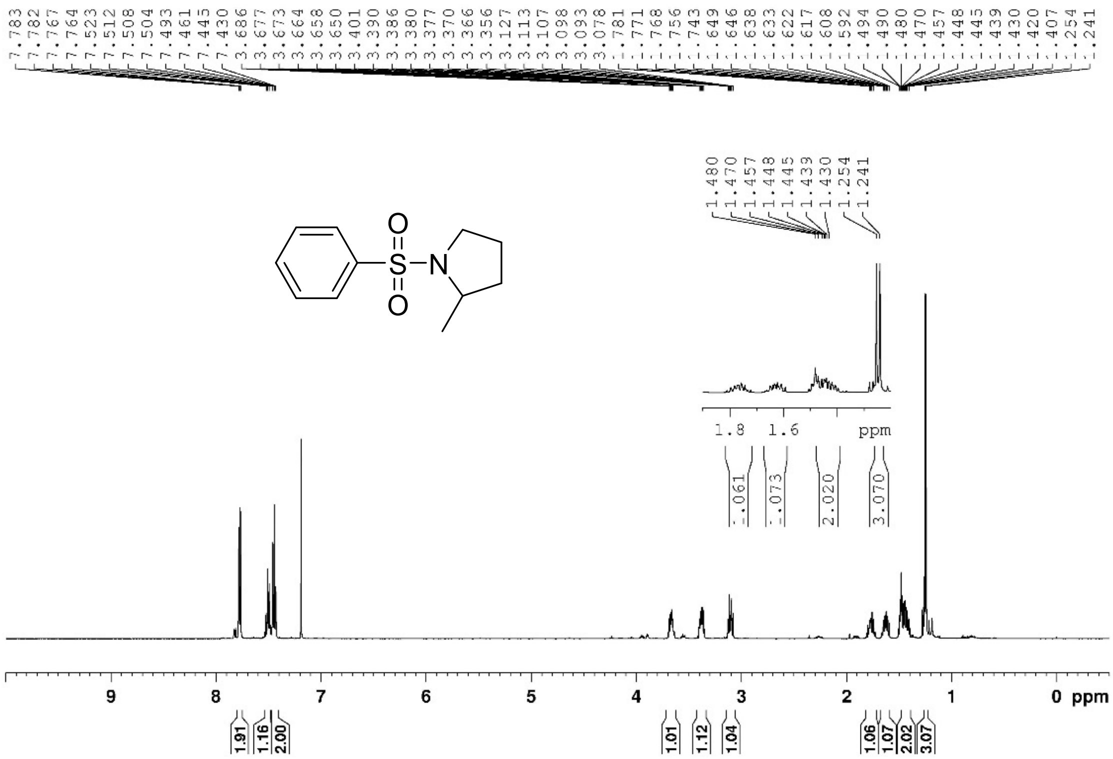
2t ^{1}H NMR (500 MHz, $CDCl_3$)



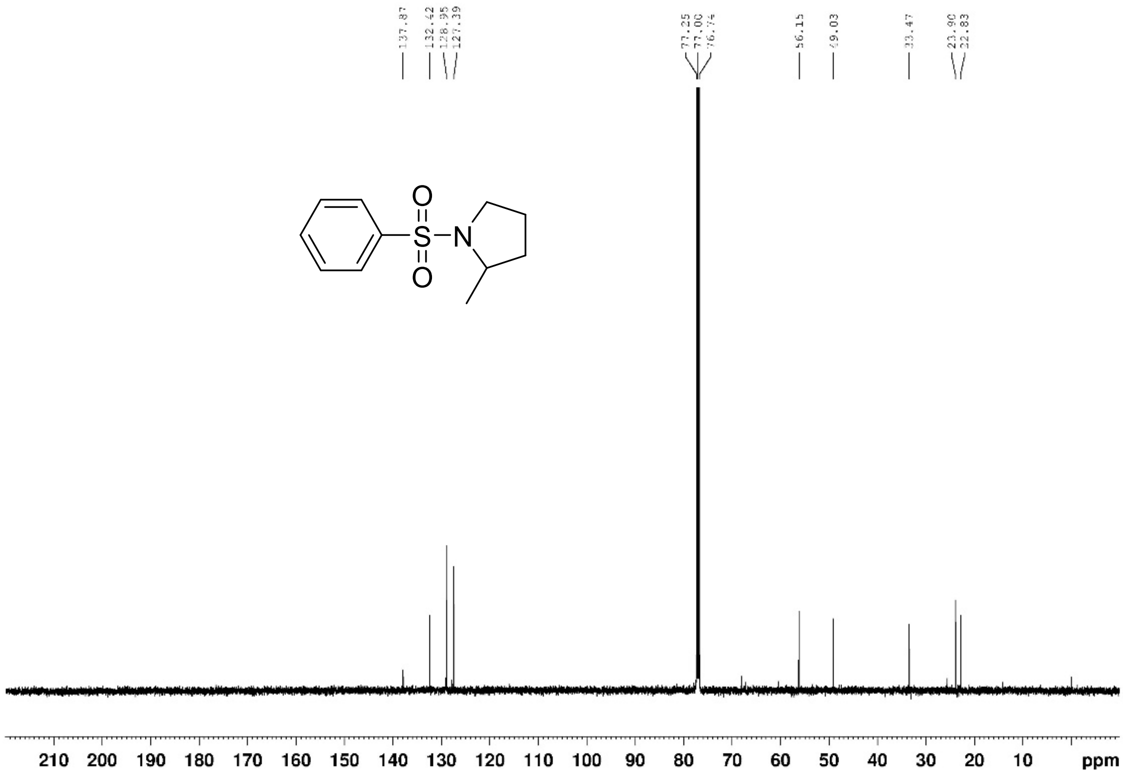
2t $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)



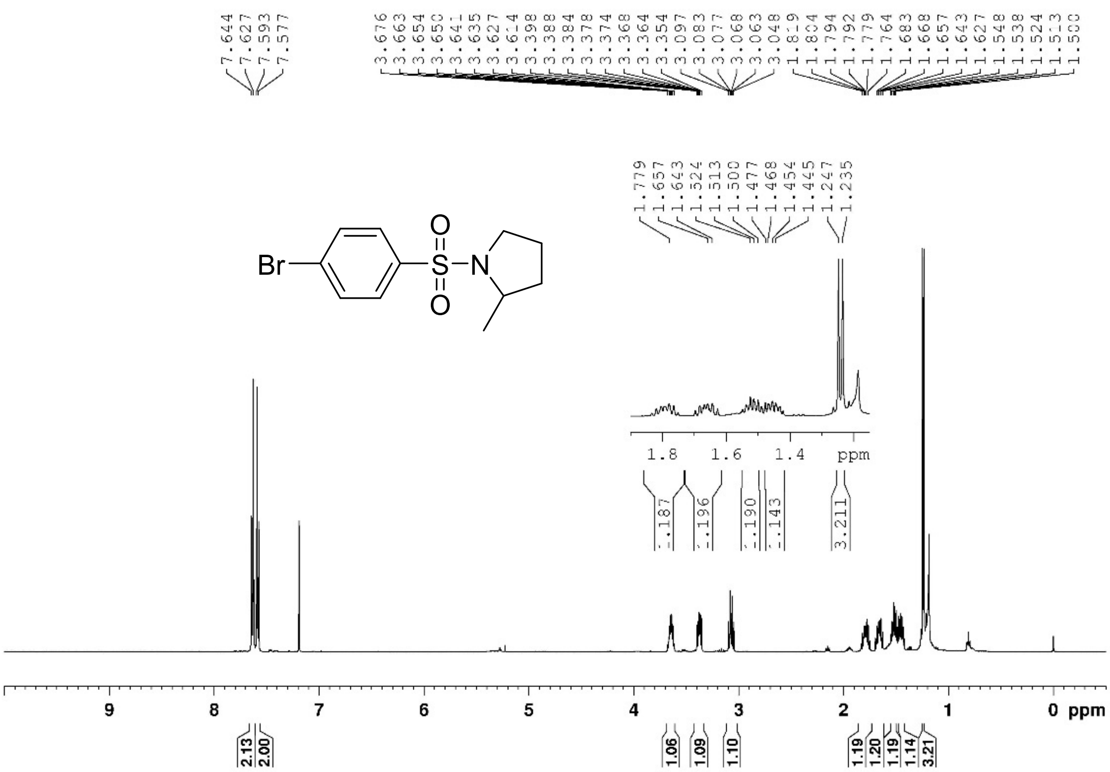
3a ^{1}H NMR (500 MHz, $CDCl_3$)



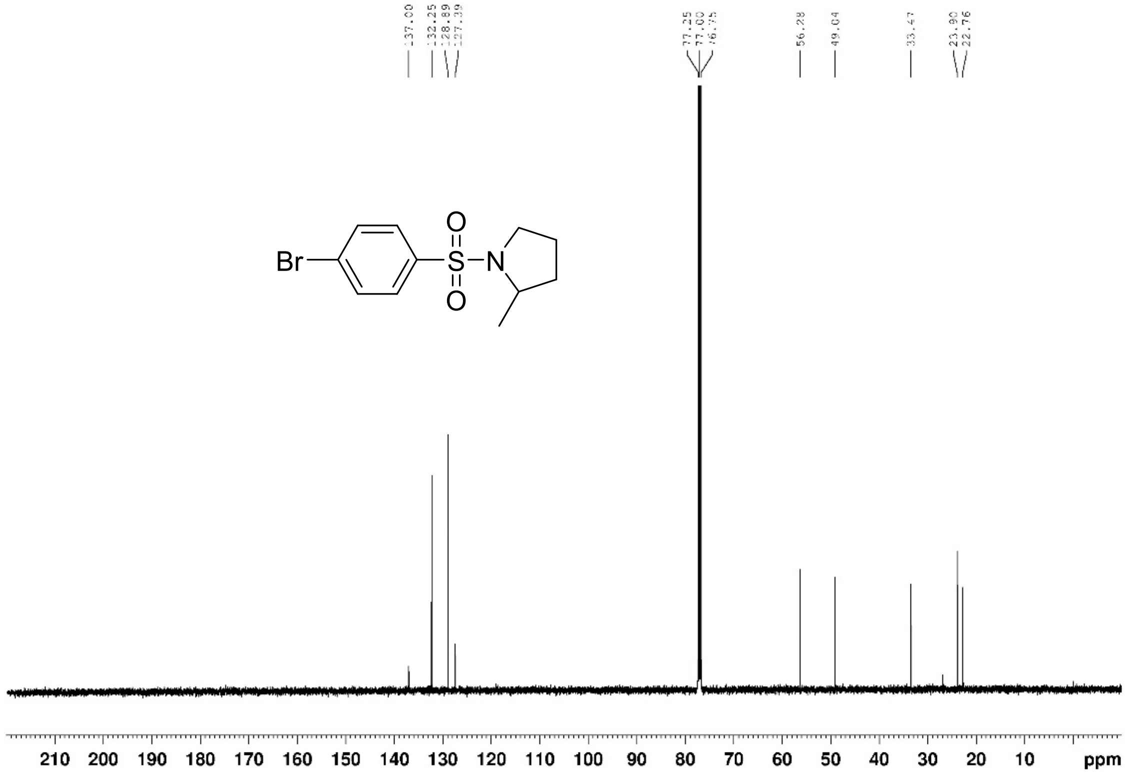
3a $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



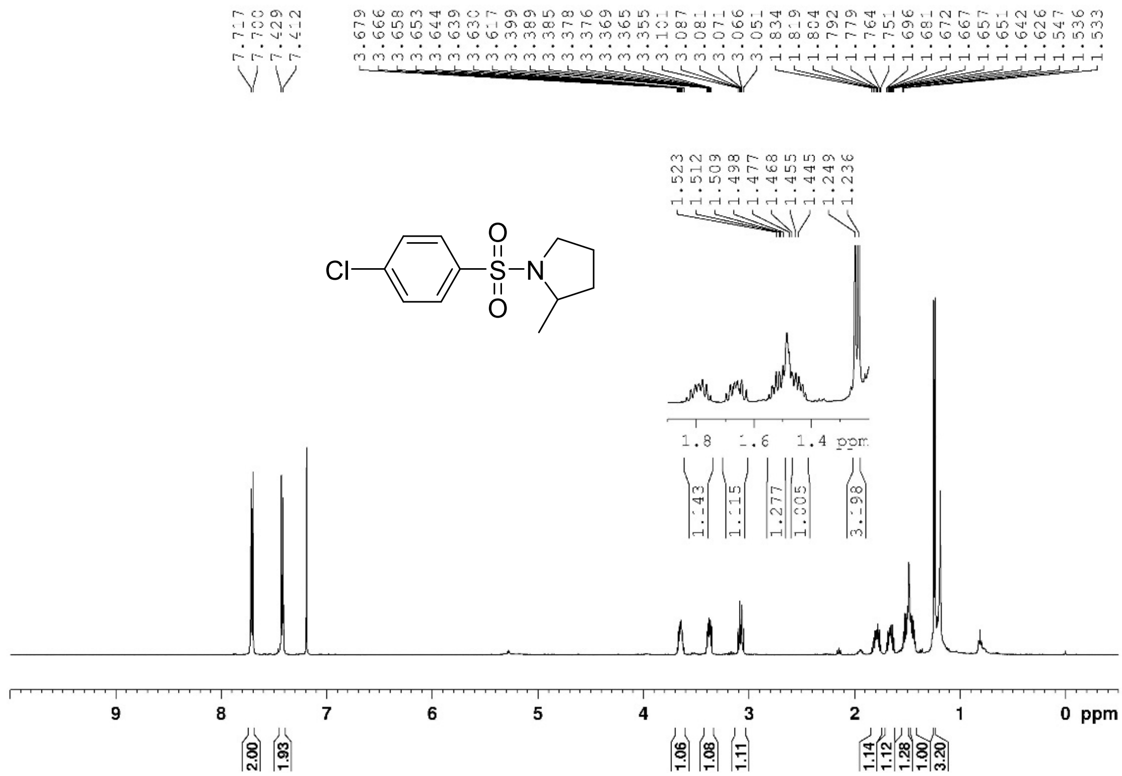
3b ^{1}H NMR (500 MHz, $CDCl_3$)



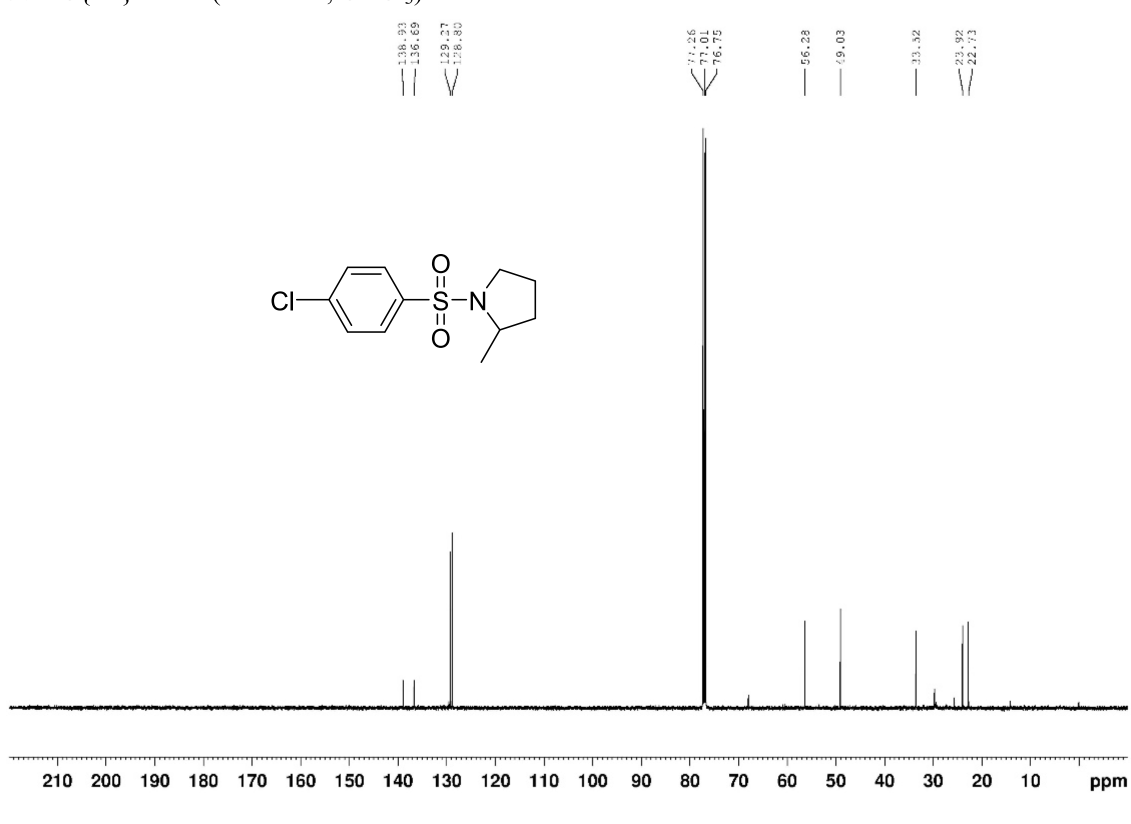
3b $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



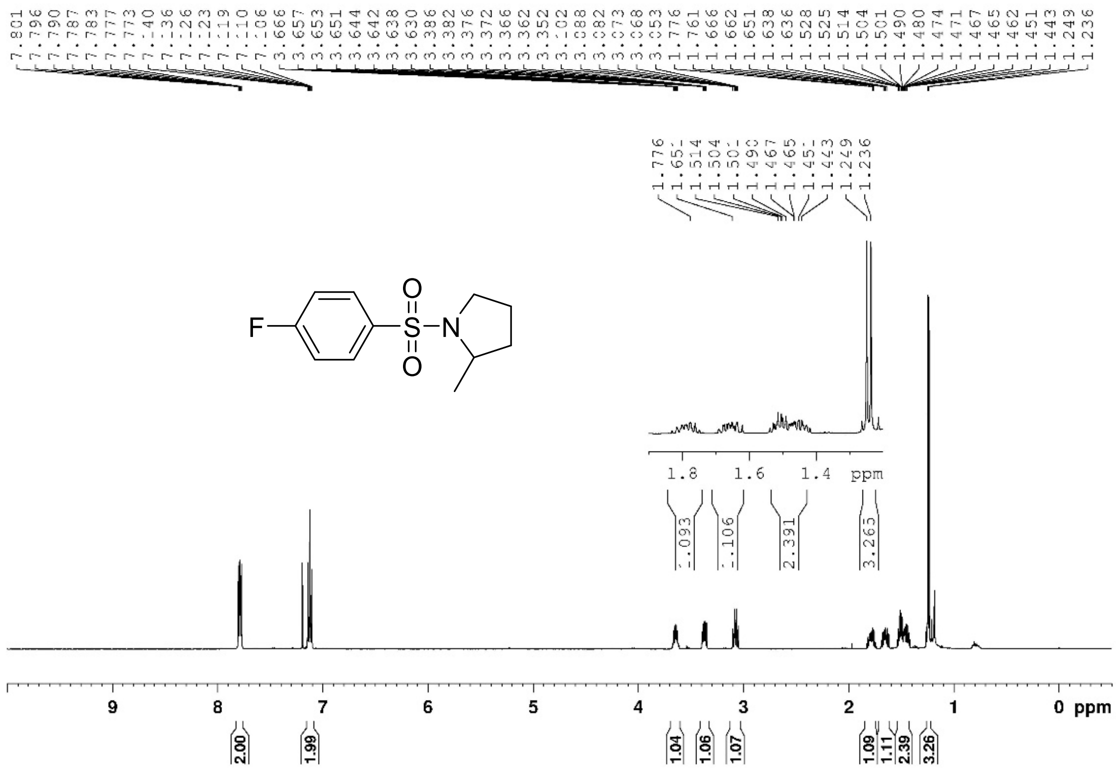
3c ^{1}H NMR (500 MHz, $CDCl_3$)



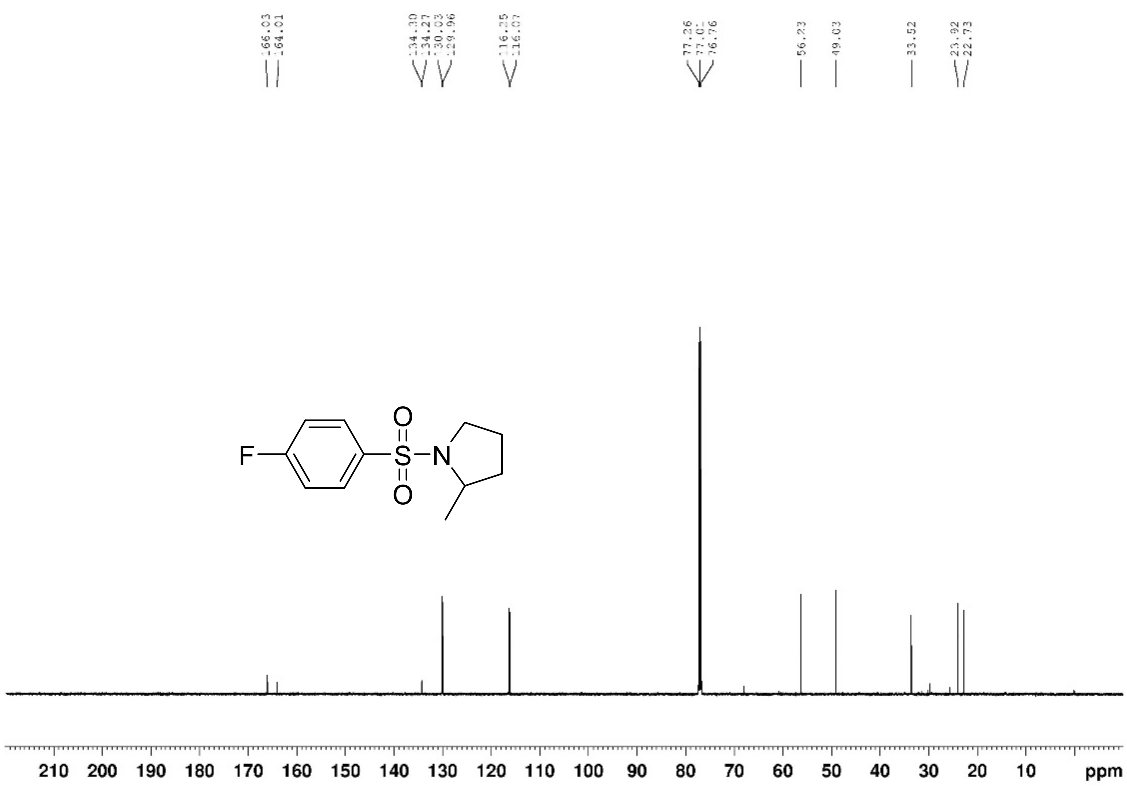
3c $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



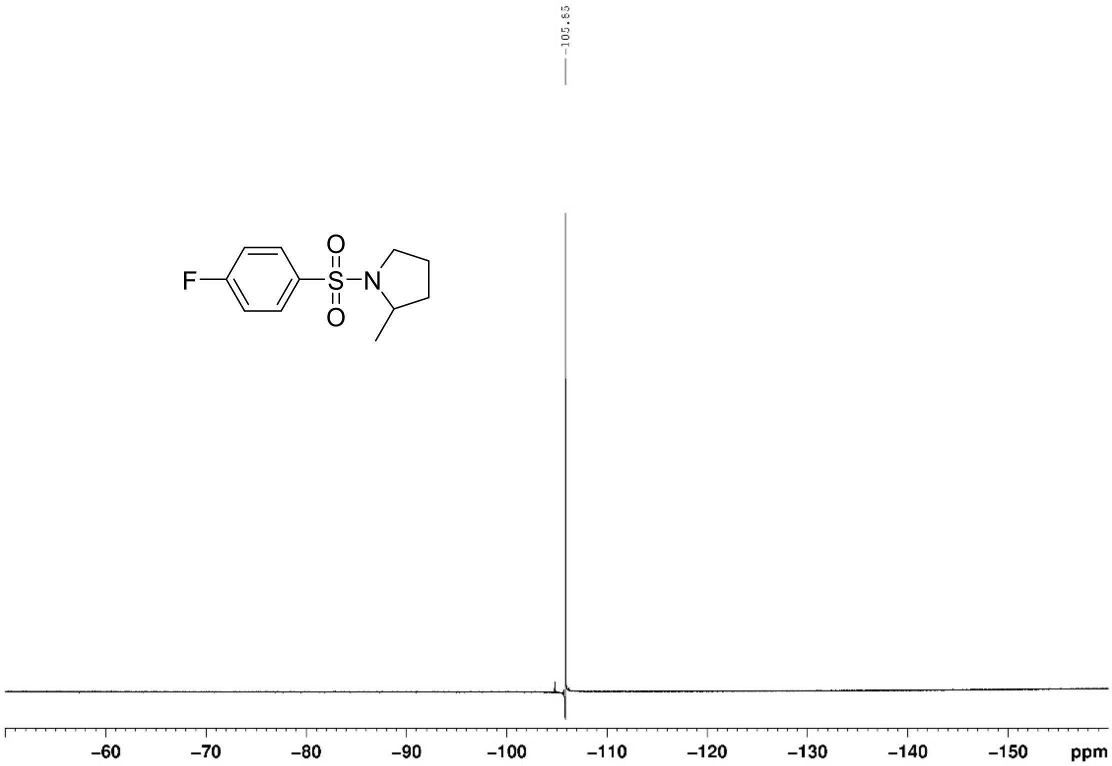
3d ^{1}H NMR (500 MHz, $CDCl_3$)



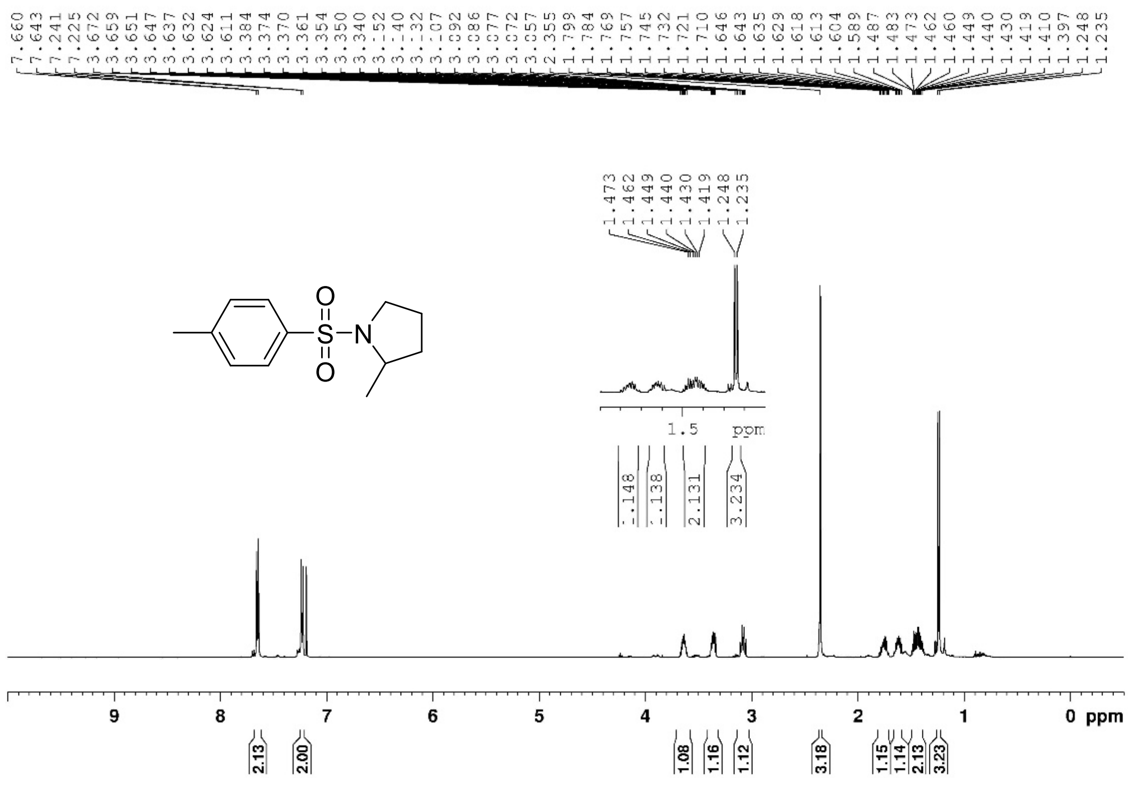
3d $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



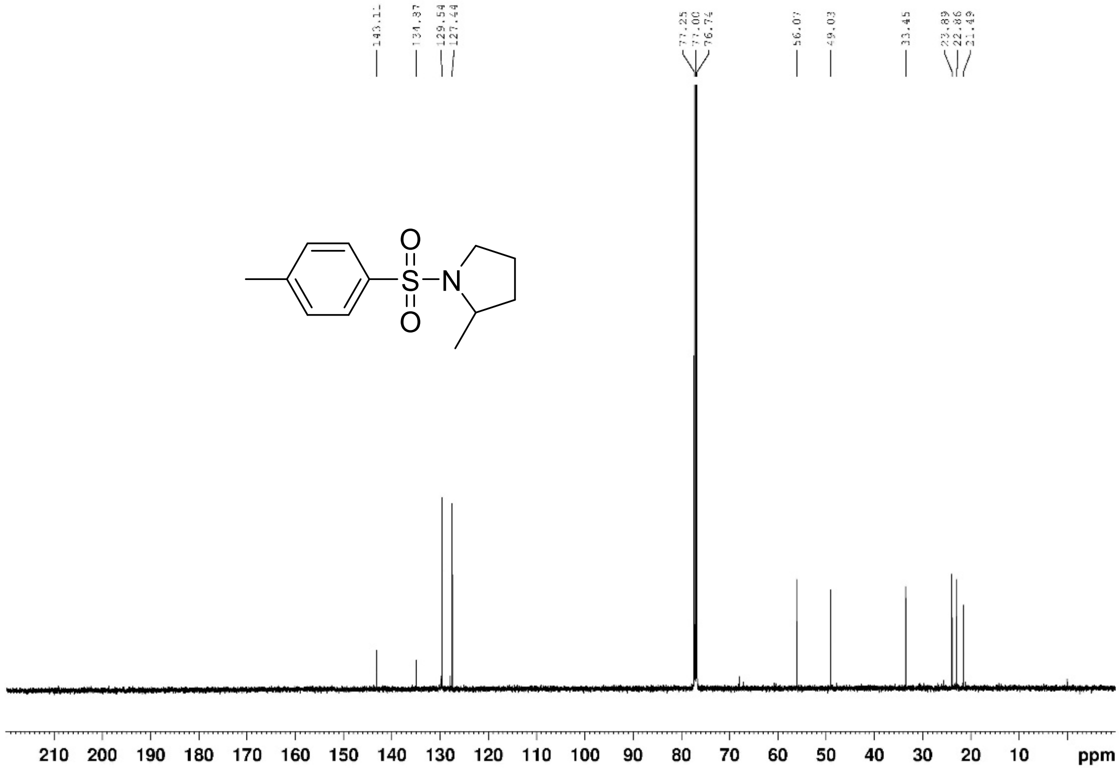
3d ^{19}F NMR (471 MHz, $CDCl_3$)



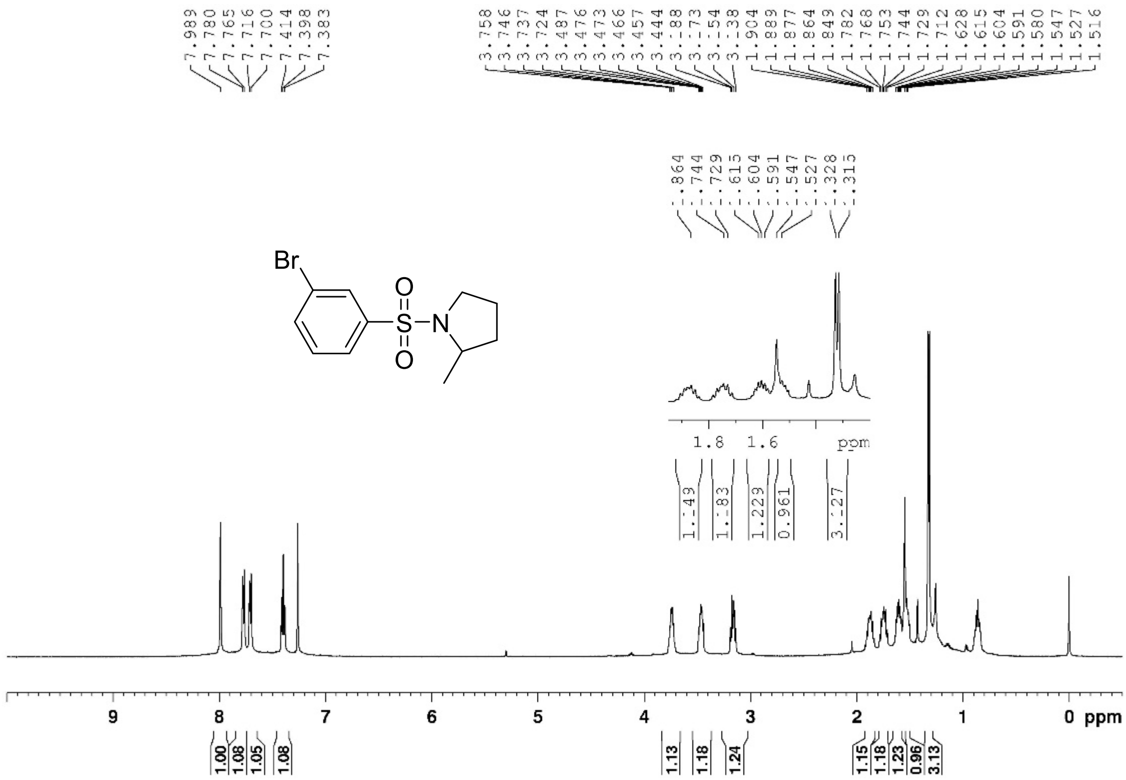
3e ^{1}H NMR (500 MHz, $CDCl_3$)



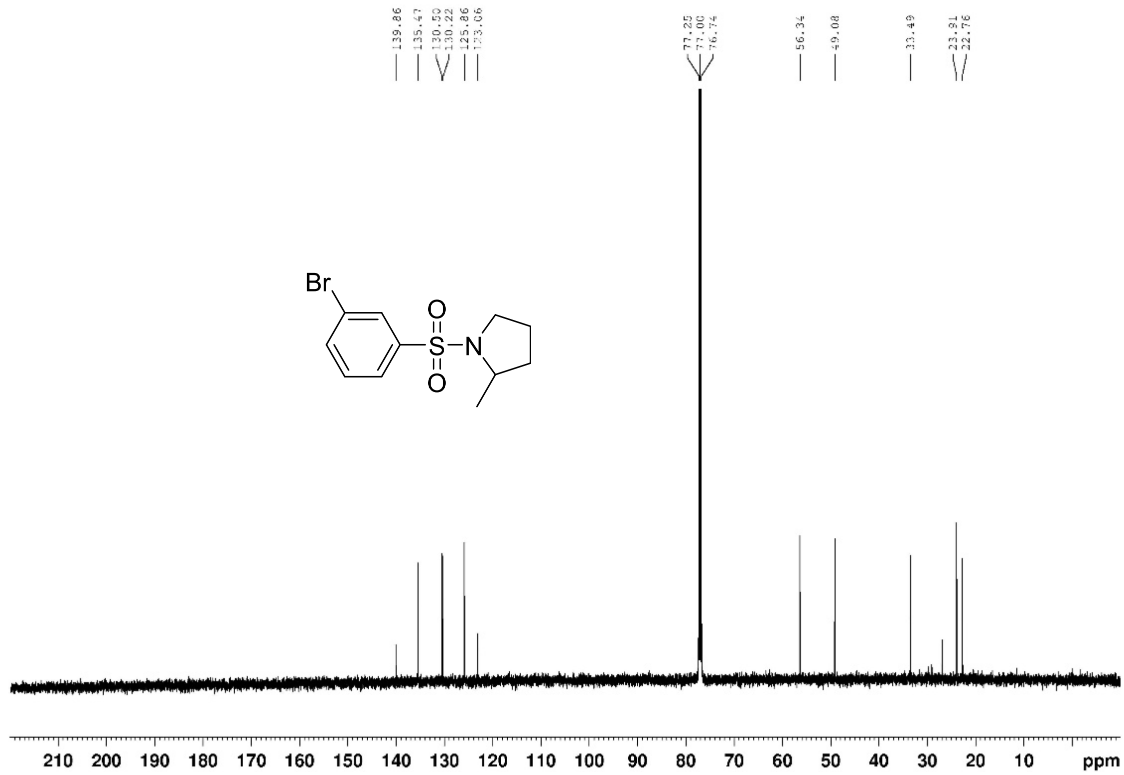
3e $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)



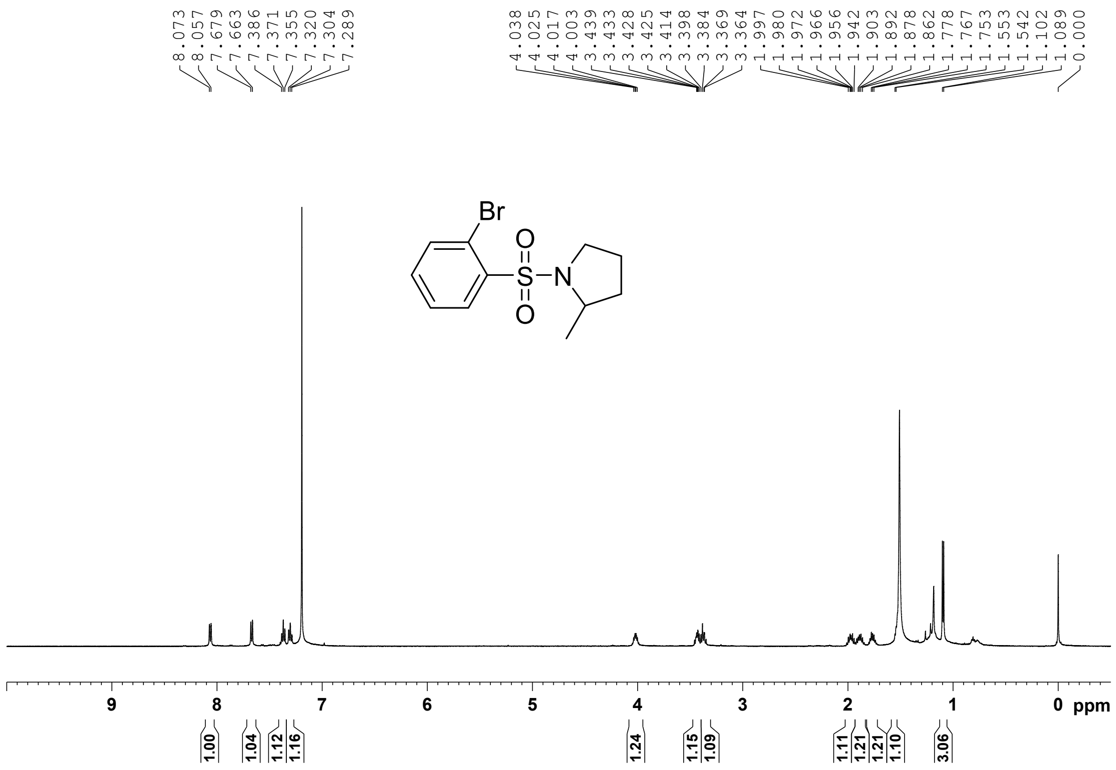
3f ^1H NMR (500 MHz, $CDCl_3$)



3f $^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$)



3g ^{1}H NMR (500 MHz, $CDCl_3$)



3g $^{13}C\{^1H\}$ NMR (126 MHz, $CDCl_3$)